



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP-1 COORDINATION

- Q1. The number of ions formed on dissociation of following complexes  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ,  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  are respectively:  
(a) 3, 0, 2 (b) 2, 3, 1 (c) 2, 3, 2 (d) 3, 1, 2
- Q2. The IUPAC name of following complex  $\text{K}_3[\text{Fe}(\text{CN})_6]$  is:  
(a) Potassium hexacyanoiron(III) (b) Potassium hexacyanoferrate(III)  
(c) Hexacyano potassiumferrate(II) (d) Potassium cyanoferrate(III)
- Q3. Which of the following ions will give test of all the ions present in it:  
(a) Mohr's salt (b)  $\text{K}_2[\text{Fe}(\text{CN})_6]$  (c)  $\text{PdCl}_4^{2-}$  (d)  $[\text{Co}(\text{Cl})_3(\text{NH}_3)_3]$
- Q4. A co-ordination complex of platinum has an empirical formula  $\text{PtCl}_3 \cdot (\text{NH}_3)_2(\text{NO}_2)$ . On reacting with excess silver nitrate, one mole of the complexes produces two moles of  $\text{AgCl}$  precipitate. The ionic formula of this complex is:  
(a)  $[\text{Pt}(\text{NO}_2)(\text{Cl})_3] \cdot (\text{NH}_3)_2$  (b)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}(\text{NO}_2)$   
(c)  $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)(\text{Cl})]\text{Cl}_2$  (d)  $[\text{Pt}(\text{NO}_2)(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$
- Q5. The IUPAC name of the complex:  
  
(a) diamminedichloroplatinum(II) (b) bis(aminechloro)platinum(II)  
(c) trans-diamminedichloroplatinum(II) (d) cis-diamminedichloroplatinum(II)
- Q6. Consider the following statements:  
A. In primary bonding, position charge of metal is balanced by (–)ve ions.  
B. In secondary bonding, molecules/ions are attached directly to metal ion.  
The correct option is:  
(a) T, F (b) T, T (c) F, F (d) F, T
- Q7. The incorrect statement regarding secondary valences are:  
(a) they are ionisable (b) attached directly to metal ion  
(c) they are non-ionisable (d) equal to the coordination number
- Q8. For the given binary compounds,  $\text{CoCl}_3$ ,  $\text{FeCl}_3$  and  $\text{PtCl}_2$ , the primary valences are:  
(a) 3, 2, 2 respectively (b) 2, 2, 2 respectively (c) 3, 3, 2 respectively (d) 0, 0, 0 respectively
- Q9. The formula for the complex "Ammonium tetrachlororuthenate (1–)"  
(a)  $[\text{Ru}(\text{NH}_3)_4]\text{Cl}$  (b)  $[\text{Ru}(\text{NH}_3)_3\text{Cl}](\text{NH}_3)$  (c)  $[\text{Ru}(\text{NH}_4^+)\text{Cl}_3]\text{Cl}$  (d)  $(\text{NH}_4^+)[\text{RuCl}_4]^-$
- Q10. The IUPAC name of  $[(\text{NH}_3)_4\text{Co}(\text{OH})(\text{NH}_2)\text{Co}(\text{NH}_3)_4]^{4+}$  is  
(a)  $\mu$ -hydroxo- $\mu$ -amidobis (tetraaminecobalt)(IV)  
(b)  $\mu$ -amido- $\mu$ -hydroxobis (tetraaminecobalt)(IV)

- (c) tetraamminecobalt- $\mu$ -amido- $\mu$ -hydroxo-tetraamminecobalt(IV)  
 (d) bis(tetraamminecobalt)- $\mu$ -amido- $\mu$ -hydroxy(IV)
- Q11. Which of the following is not a double salt:  
 (a)  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (b)  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (c)  $\text{KLi}[\text{Fe}(\text{CN})_6]$  (d)  $\text{Fe}_2(\text{SO}_4)_3$
- Q12. The IUPAC name of  $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]^{2+}$  is:  
 (a) tri (2,2'-bipyridine) ferrate(II) (b) tris (2, 2'-bipyridine) iron(II)  
 (c) di-(2,3-bipyridine) iron(III) (d) tris (2,2'-bipyridine) iron(II)
- Q13. When  $\text{AgNO}_3$  is added to a solution of  $\text{Co}(\text{NH}_3)_4 \cdot \text{Cl}_3$ , one chlorine satisfy primary valency and two chlorines satisfy both primary and secondary valences. This means the formula of complex is:  
 (a)  $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2$  (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (c)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot \text{NH}_3$  (d)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_2]\text{Cl}_2 \cdot (\text{NH}_3)$
- Q14. The IUPAC nomenclature of  $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$  is:  
 (a) dichlorobis(ethylenediamine) cobalt(III) (b) bis(ethylenediamine) dichlorocobalt(I)  
 (c) dichlorobis(ethylenediamine) cobalt(I) (d) bis(ethylenediamine) dichlorocobalt(III)
- Q15. A complex is composed of one chromium, three bromides and six water molecules. Upon addition of excess  $\text{AgNO}_3$ , 1.0g aqueous solution of a complex gave 0.94g of  $\text{AgBr}$ . The molecular formula of complex is: (Atomic height: Cr = 52, Br = 80, Ag = 108, H = 1, O = 16)  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$  (b)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$  (c)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]\text{Br} \cdot 2\text{H}_2\text{O}$  (d)  $[\text{Cr}(\text{H}_2\text{O})_3\text{Br}_3] \cdot 3\text{H}_2\text{O}$
- Q16. Considering Werner theory, which of the following statement is/are correct:  
 (a) Ligands directly attached to metal are also known as secondary valences  
 (b)  $[\text{Co}(\text{Cl})_3(\text{NH}_3)]$  gives no precipitate when treated with excess  $\text{AgNO}_3$  solution  
 (c) Primary valences are ionisable (d)  $\text{CrCl}_3$  has two primary valences
- Q17. Which of the following statements is true:  
 (a)  $\text{CoCl}_3$  is having three primary valences (b) Mohr's salt is a complex  
 (c) Complexes dissociate completely into ions in solution (d)  $[\text{Co}(\text{NH}_3)_6] \cdot 3\text{Cl}^-$  has six secondary valences
- Q18. Among the following which is incorrect combination:  
 (a) Hexaamine cobalt(III) hexacyanochromate(III) –  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$   
 (b) Pentaammine (thiocyano – S) cobalt(III) chloride –  $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$   
 (c)  $\text{Na}[\text{PCl}_6]$  – Sodium hexachlorophosphate(V)  
 (d)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  – Tripotassium hexacyanoferrate(III)
- Q19. Find the incorrect number of statement(s):  
 (I)  $[\text{Fe}(\text{NH}_3)_6] \cdot 3(\text{Cl})$  gives three ions in solution.  
 (II)  $\text{Fe}(\text{SO}_4)(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  dissociates completely in ions in aqueous solution.  
 (III)  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}$  gives white ppt with  $\text{AgNO}_3$  solution.  
 (IV)  $\text{PtCl}_2$  has no primary valences.
- Q20. Among the following, how many complexes gives three ions in solution:  
 (a)  $[\text{Fe}(\text{NH}_3)_5\text{Cl}] \cdot 2\text{Cl}$ , (b)  $\text{Fe}(\text{SO}_4)_2 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ,  
 (c)  $[\text{CoCl} \cdot (\text{NH}_3)_4]\text{Cl}_2$ , (d)  $\text{K}_3[\text{Fe}(\text{CN})_6]$

## ANSWERS

- 1 a    2. b    3.a    4. c    5. c    6. b    7. a    8. c    9.d    10. B    11. c    12. b  
 13.b    14. a    15. b    16. a, b, c    17. a, d    18. b, d    19. 2    20. 2

## HINTS AND SOLUTIONS

1 a

Sol:  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \Rightarrow 2\text{Cl}^-$  and one  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \Rightarrow$  zero ions $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \Rightarrow$  one  $\text{Cl}^-$  and one  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ 

2. b

Sol: The anionic complexes ends with the suffix 'ate' potassium hexacyanoferrate(III)

3. a

Sol: Only double salts dissociate completely into ions hence gives test for all the ions present in them.

4. c

Sol: For formation of two mole of  $\text{AgCl}$  precipitate, two ionizable  $\text{Cl}^-$  ions should be present. Therefore, the ionic formula of complex is  $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)\text{Cl}]\cdot\text{Cl}_2$ 

5. c

Sol: Prefix designating adjacent (cis-) and opposite (trans-) geometric locations are added while naming the complex.

6. b

Sol: Primary bonding  $\Rightarrow$  (+)ve charge of metal is balanced by (-)ve ionsSecondary bonding  $\Rightarrow$  molecules/ligands are attached directly to metal ion

7. a

Sol: Secondary valences are non-ionizable and are equal to the coordination number.

8. c

Sol: Primary valences are the those which balance the (+)ve charge of metal ion.

9. d

Sol:

10. b

Sol: Bridging ligands between two metal ions is represented by prefix- ' $\mu$ '

11. c

Sol: Double salts dissociate completely into respective ions.

12. b

Sol:  $\text{C}_{10}\text{H}_8\text{N}_2 \rightarrow$  2, 2'-bipyridine $\therefore [\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]^{2+}$  is tris (2,2'-bipyridine) iron(II)

13 b

Sol: One primary valency means one  $\text{Cl}^-$  is ionizable which indicates the formula of complex is  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

In this formula only, two  $\text{Cl}^-$  are satisfying primary as well as secondary valences and one  $\text{Cl}^-$  is satisfying primary valence only.

14 a

Sol: The IUPAC name of  $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$  is dichlorobis (ethylenediamine) cobalt(III).

15 b

Sol: Molecular mass of the complex  $\text{CrBr}_3 \cdot (\text{H}_2\text{O})_6 = 52 + 3(80) + 6(18) = 400 \text{ g/mol}$

Molecular mass of  $\text{AgBr} = 108 + 80 = 188 \text{ g/mol}$

$$\text{moles of } \text{Cr}(\text{Br})_3(\text{H}_2\text{O})_6 = \frac{\text{given wt.}}{\text{molar wt.}} = \frac{1}{400} = 2.5 \times 10^{-3} \text{ mol}$$

$$\text{moles of } \text{AgBr} = \frac{0.94}{188} = 5 \times 10^{-3} \text{ mol}$$

Moles of  $\text{AgBr} = 2[\text{moles of } \text{Cr}(\text{Br})_3(\text{H}_2\text{O})_6]$

This means 2  $\text{Br}^-$  ligands are present outside the coordination sphere which are responsible for  $\text{AgBr}$  precipitation.

Therefore, complex is  $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$

16 a,b,c

Sol: • Secondary valences are attached directly to the metal ion.

•  $[\text{Co}(\text{Cl})_3(\text{NH}_3)]$ , no  $\text{Cl}^-$  outside coordination sphere hence no ppt formation.

• Primary valences are ionisable

•  $\text{CrCl}_3$  has three primary valences.

17 a, d

Sol: • Mohr's salt is a double salt

• Complexes donot dissociate completely into ions in solution

18 b, d

Sol:  $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$  – Pentaammine (thiocyano – N) cobalt(III) chloride

$\text{K}_3[\text{Fe}(\text{CN})_6]$  – Potassium hexacyanoferrate(III)

19 2

Sol: •  $[\text{Fe}(\text{NH}_3)_6] \cdot 3\text{Cl}$  gives 4 ions in solution,  $3\text{Cl}^-$  and one  $[\text{Fe}(\text{NH}_3)_6]^{3+}$

•  $\text{PtCl}_2$  has two primary valences.

20 2

Sol: (a) 3 ions

(b) dissociates completely  $\Rightarrow$  more than three ions

(c) 3 ions

(d) 4 ions





# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

---

## DPP-2 COORDINATION

---

- Q1. The complexes  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$  represent an example of:  
(a) ligand isomerism (b) linkage isomerism  
(c) coordination isomerism (d) ionization isomerism
- Q2. The existence of two different coloured complexes of  $\text{Co}(\text{NH}_3)_4\text{Cl}_2$  is due to:  
(a) optical isomerism (b) linkage isomerism  
(c) geometrical isomerism (d) coordination isomerism
- Q3. The complex  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_2$  and  $[\text{CoCH}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$  is an example of  
(a) linkage isomer (b) positional isomer (c) ionization isomer (d) optical isomer
- Q4. Select the incorrect match:  
(a)  $[\text{PtCl}(\text{NCS})(\text{NH}_3)_2]$ ,  $[\text{PtCl}(\text{SCN})(\text{NH}_3)_2]$  – linkage isomerism  
(b)  $[\text{Co}(\text{1,2-diaminopropane})_2\text{Cl}_2]^+$ ,  $[\text{Co}(\text{1,3-diaminopropane})_2\text{Cl}_2]^+$  – coordination isomerism  
(c)  $[\text{Ni}(\text{CN})(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}$ ,  $[\text{NiCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{CN}$  – ionization isomerism  
(d) None of these
- Q5. The compounds pentaaminesulphatocobalt(III) bromide and pentaaminesulphatocobalt(III) iodide represent:  
(a) linkage isomerism (b) ionization isomerism (c) ligand isomerism (d) no isomerism
- Q6. The complexes  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_2)]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{ONO})]\text{Cl} \cdot \text{H}_2\text{O}$  is an example of:  
(a) hydrate isomerism (b) linkage isomerism (c) ionization isomerism (d) all of these
- Q7.  $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Cl}$  and  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Br}$  can be distinguished by/ and isomerism shown is:  
(a)  $\text{BaCl}_2$ , ionization (b)  $\text{AgNO}_3$ , ionization (c)  $\text{AgNO}_3$ , coordinate (d)  $\text{BaCl}_2$ , linkage
- Q8. The ionization isomer of  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{Cl}$  is  
(a)  $[\text{Co}(\text{NH}_3)_4(\text{O}_2\text{N})]\text{Cl}_2$  (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_2)$   
(c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{ONO})]\text{Cl}$  (d)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2(\text{NO}_2)]\text{H}_2\text{O}$
- Q9. The total possible coordination isomers for the following compounds respectively are:  
 $[\text{Co}(\text{en})_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$   
 $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$   
(a) 4, 4 (b) 2, 2 (c) 2, 4 (d) 4, 2
- Q10. The isomerism that are possible in the Co(III) complexes  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$  and  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  respectively are:  
(a) coordination and position (b) optical and linkage  
(c) geometrical and linkage (d) optical and optical
-

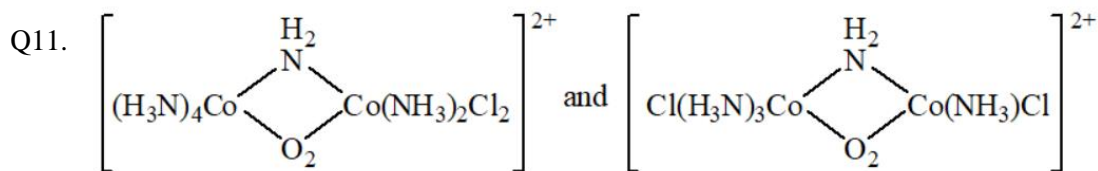


exhibit which type of isomerism:

- (a) position isomerism (b) linkage isomerism  
(c) ligand isomerism (d) ionization isomerism
- Q12. Which of the following is an example of coordination isomerism?  
(a)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
(b)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$   
(c)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  and  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\cdot\text{Cl}_2\cdot\text{H}_2\text{O}$   
(d)  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  and  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$
- Q13. The correct options about the complex  $[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]^+$  are:  
(a) IUPAC name of complex is diamminetetraisothiocyanatochromate(III)  
(b) it shows geometrical isomerism  
(c) it shows linkage isomerism  
(d) it shows ligand isomerism
- Q14. In bis (dimethylglyoximate) nickel(II), which of the following statement is/are correct:  
(a) there are 4 Ni–N bonds (b) there are 2, 5 membered rings  
(c) there are no Ni–O bonds (d) intramolecular H-bonding is present
- Q15. The number of complexes that show linkage isomerism is:  
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ ,  $[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]^+$ ,  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ ,  $[\text{Ni}(\text{CN})(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}$

### ANSWERS

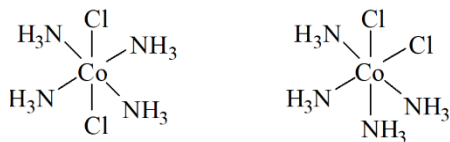
1. (d) 2. (c) 3. (c) 4.(b) 5.(d) 6. (d) 7. (b) 8. (b) 9. (d) 10. (c) 11. (a) 12. (d) 13. (a,b,c)  
14. (a, b, c, d) 15. (2)

## HINTS AND SOLUTIONS

1. (d)

Sol: This is an example of ionization isomerism because it involves exchange of ligands between coordination sphere and ionization sphere.

2. (c)



Sol:

Therefore, These two are geometrical isomers.

Correct option is (c)

3. (c)

Sol: The complexes are ionization isomers because these involve exchange of ligand between ionization sphere and coordination sphere

4. (b)

Sol:  $[\text{Co}(\text{1,2-diaminopropane})_2\text{Cl}_2]^+$  and  $[\text{Co}(\text{1,3-diaminopropane})_2\text{Cl}_2]^+$  are example of ligand isomerism. Which arise when donor site present in two different places of similar type of ligand.

5. (d)

Sol:  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br} \Rightarrow$  this is not any kind isomerism

- because there is no exchange between ionization and coordination sphere ligands
- no linkage isomerism
- no coordination and ligand isomerism

6. (d)

Sol: • the transfer of  $\text{H}_2\text{O}$  from coordination sphere to ionization sphere represents it is both hydrate and ionization sphere  
 •  $\text{NO}_2$  is coordinating with different atoms in both the complexes hence linkage isomerism

7. (b)

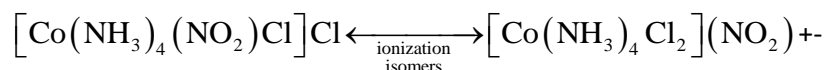
Sol:  $\text{AgCl} \rightarrow$  white ppt.

$\text{AgBr} \rightarrow$  Pale yellow ppt.

and there is exchange of ligands between coordination sphere and ionization sphere.

8. (b)

Sol: Ionization isomerism involves exchange of ligands between coordination and ionization sphere



9. (d)

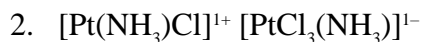
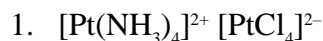
Sol: 1.  $[\text{Co}(\text{en})_3]^{3+} [\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

2.  $[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)]^{1+} [\text{Cr}(\text{C}_2\text{O}_4)_2(\text{en})]^{1-}$

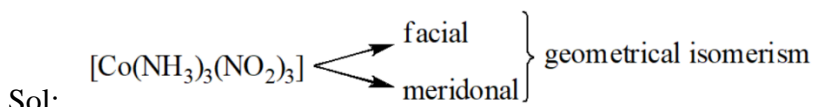
3.  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{en})_2]^{1+} [\text{Co}(\text{C}_2\text{O}_4)_2(\text{en})]^{1-}$

4.  $[\text{Cr}(\text{en})_3]^{3+} [\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

and



10. (c)



11. (a)

Sol: Position isomerism is exhibited by that complex which have bridging and non-bridging ligands and they are coordinated differently around metal atom.

12. (d)

Sol: a  $\rightarrow$  ionization isomerism

b  $\rightarrow$  linkage isomerism

c  $\rightarrow$  hydrate isomerism

d  $\rightarrow$  coordination isomerism

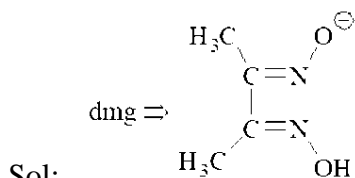
13. (a,b,c)

Sol: • IUPAC name – diamminetetraisoithiocyanatochromate(III)

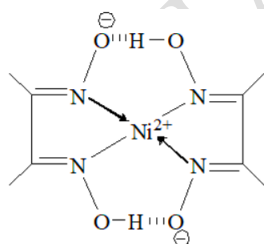
• geometrical isomerism possible (cis/trans)

• NCS  $\Rightarrow$  ambidentate ligand  $\rightarrow$  linkage isomerism possible

14. (a, b, c, d)



bis(dimethylglyoximato) nickel(II)  $\Rightarrow$



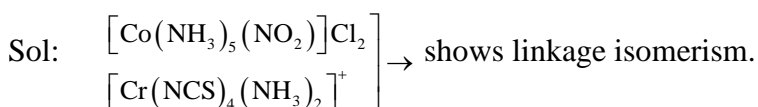
• 4  $\Rightarrow$  Ni–N bonds

• Zero  $\Rightarrow$  N–O bonds

• Two 5-membered rings present

• intramolecular hydrogen bonding present

15. (2)





# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

---

## DPP-3 COORDINATION

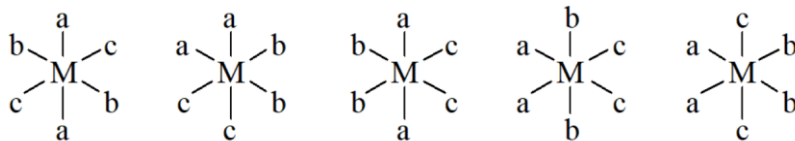
---

- Q1. The number of possible isomers for the octahedral complex ion  $[\text{Co}(\text{en})\text{Cl}_2(\text{NH}_3)_2]^+$   
(a) 2 (b) 4 (c) 6 (d) 8
- Q2. The number of total isomers of the complex  $[\text{Pd Cl}_2(\text{I})(\text{Br})]^{2-}$   
(a) 2 (b) 3 (c) 0 (d) 4
- Q3. The number of geometrical isomers for a complex  $\text{Ma}_3\text{b}_2\text{c}$  type are—  
(a) 2 (b) 4 (c) 3 (d) 6
- Q4. For a complex  $[\text{Pt}(\text{NH}_3)_2(\text{Py})_2\text{Cl}_2]^{2+}$ , total number of stereoisomer are  
(a) 5 (b) 6 (c) 4 (d) 7
- Q5. For the complex  $\text{Mo}(\text{C}_5\text{H}_5\text{N})_3(\text{CO})_3$ , how many isomers will be there  
(a) 2 (b) 3 (c) 1 (d) 4
- Q6. The number of stereoisomers for  $[\text{Co}(\text{gly})_3]^{3+}$  and  $[\text{Co}(\text{en})_3]^{3+}$  respectively are  
(a) two and two (b) four and two (c) two and four (d) four and zero
- Q7. Among the following complexes,  
(i)  $[\text{Ru}(\text{bpy})_3]^+$  (ii)  $\text{Cr}[\text{EDTA}]^-$   
(iii)  $\text{trans}-[\text{CrCl}_2(\text{oxalate})_2]^{3-}$  (iv)  $\text{cis}-[\text{CrCl}_2(\text{oxalate})_2]^{3-}$   
The one that shows chirality  
(a) (i), (ii) (b) (ii), (iii), (iv) (c) (i), (iii), (iv) (d) (i), (ii), (iii)
- Q8. The complex that exists as a pair of enantiomers is  
(a)  $\text{trans}-[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$  (b)  $\text{cis}-[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$   
(c)  $[\text{Pt}(\text{PPh}_3)(\text{Cl})(\text{Br})(\text{CH}_3)]^-$  (d)  $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$
- Q9. The number of possible isomers for  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$  is (bpy = 2,2'-bipyridine)  
(a) 2 (b) 3 (c) 4 (d) 5
- Q10. The type of complex that has zero stereoisomers:  
(a)  $\text{Ma}_4$  (b)  $\text{Ma}_3\text{b}$  (c)  $\text{Ma}_6$  (d)  $\text{Ma}_4\text{bc}$
- Q11. Which of the following statement is not true for the complex  $[\text{Pt}(\text{Br})(\text{NO}_2)(\text{bpy})_2]^+$   
(a) only cis isomer shows optical activity  
(b) it has three geometrical isomers cis & trans  
(c) cis and trans are not diastereomers to each other  
(d) cis and trans are diastereomers to each other

Q12. Which of the following complex exhibit geometrical isomerism:

- (a)  $\text{Ma}_3\text{bcd}$  (b)  $\text{Ma}_5\text{b}$  (c)  $\text{Mabcd}$  (d)  $\text{Ma}_6$

Q13. The number of geometrical isomers for  $\text{Ma}_2\text{b}_2\text{c}_2$  type complex is \_\_\_\_\_.



Q14. How many complexes will exist as enantiomeric pairs:

$\text{Ma}_2\text{bcde}$ ,  $\text{Ma}_4\text{b}_2$ ,  $\text{Ma}_3\text{b}$ ,  $\text{Ma}_2\text{b}_2$ ,  $\text{Ma}_3\text{b}_3$ ,  $\text{Ma}_6$ ,  $\text{Ma}_2\text{b}_2\text{c}_2$

Q15. The sum of total stereoisomers for  $\text{Mabcd}$  and  $\text{Mabcdef}$  type complexes is \_\_\_\_\_.

### ANSWERS

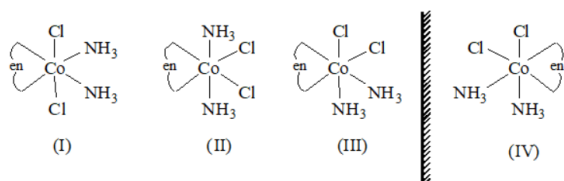
1.(b) 2.(a) 3.(c) 4.(b) 5.(a) 6.(b) 7.(d) 8.(d) 9.(b) 10.(a, b, c) 11.(b, c) 12.(a, c)

13.(5) 14. (2) 15.(33)

## HINTS AND SOLUTIONS

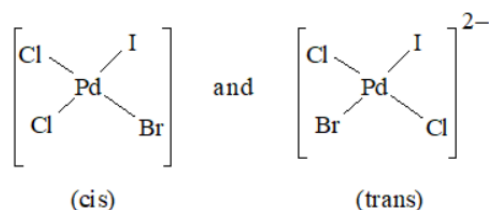
1. (b)

Sol: Total 4 possible isomers.

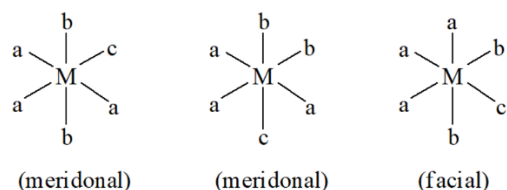


2. (a)

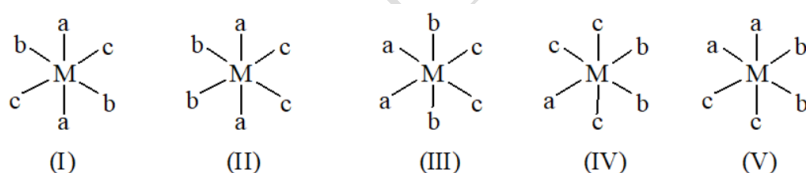
Sol: This is a square planar complex which can show cis and trans-isomerism–



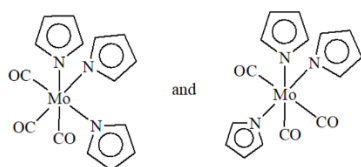
3. (c)

Sol:  $\therefore$  3 geometrical isomers.

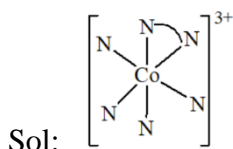
4. (b)

Sol: Let us consider this as  $Ma_2b_2c_2$  type of molecule for the sake of simplicity.(V) is optically active hence, total no. stereoisomers will be  $5 + 1 \Rightarrow 6$ 

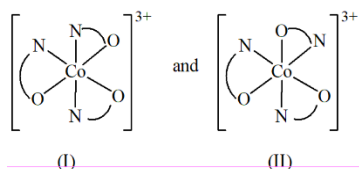
5. (a)

Sol:  $MA_3B_3$  type complexes do not show optical isomerism because these type of complexes contain plane of symmetry. Therefore, two isomers will be possible.

6. (b)



$\Rightarrow$  do not have any POS so, this molecule and its enantiomeric pair  $\Rightarrow 1 + 1 \Rightarrow 2$  stereoisomers.

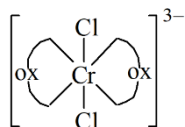


(I) and (II) both do not have any plane of symmetry, so their enantiomeric forms will also exist.

$\therefore 2 + 2 \Rightarrow 4$  stereoisomers

7. (d)

Sol:  $\Rightarrow$  This complex has plane of symmetry, so it won't be chiral

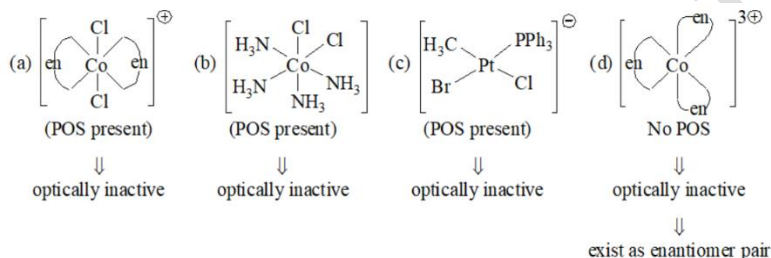


All other complexes have no symmetry plane and hence chiral

$\therefore$  (i), (ii) and (iii) are chiral.

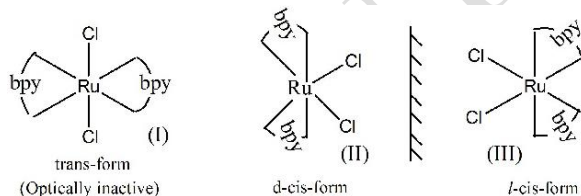
8. (d)

Sol: The complex which is optically active will exist as a pair of enantiomer.



9. (b)

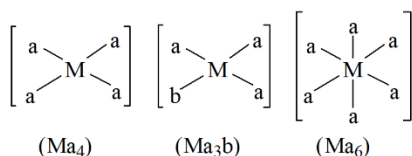
Sol: Isomers of  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$  can be represented as



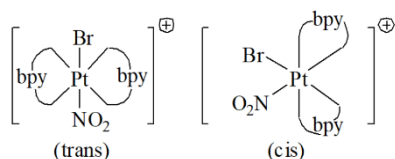
II and III are enantiomers.

10. (a, b, c)

Sol: (a), (b) and (c) have no stereoisomers, because no isomers are possible for these complexes as the connectivity is going to be same.



11. (b, c)



Sol:



cis form is optically active because no POS.

cis and trans forms are diastereomers to each other.

it has two geometrical isomers (cis/trans) and 3 stereoisomers.

Incorrect statements are 12. (a, c)

Sol:  $\text{Ma}_3\text{bcd}$  and  $\text{Mabcd}$  exhibit geometrical isomerism because in  $\text{Ma}_5\text{b}$  and  $\text{Ma}_6$ , no different arrangement / connectivity is possible

13. (5)

14. (2)

Sol:  $\left. \begin{array}{l} \text{Ma}_2\text{bcde} \\ \text{Ma}_2\text{b}_2\text{c}_2 \end{array} \right\} \rightarrow \text{exist as enantiomeric pairs}$

All other have POS hence do not exist as enantiomeric pairs

15. (33)

Sol: Total stereoisomers:

for  $\text{Mabcd} \Rightarrow 3$

for  $\text{Mabcdef} \Rightarrow$

15	+	15	= 30
↓		↓	
geometrical isomers		enantiomers pairs	

Total sum of stereoisomers  $\Rightarrow 30 + 3 \Rightarrow 33$

.....



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

---

## DPP-4 COORDINATION

---

- Q1. Which of following do not exist on basis of electroneutrality principle  
(a)  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  (b)  $[\text{NiF}_6]^{4-}$  (c)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{CoCl}_6]^{4-}$
- Q2. Arrange the compound in increasing order of thermodynamic stability.  
(i)  $[\text{Na}(\text{H}_2\text{O})_6]^+$  (ii)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  (iii)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  (iv)  $\text{SF}_6$   
(a) (iv) > (iii) > (ii) > (i) (b) (iii) > (ii) > (i) > (iv)  
(c) (i) > (ii) > (iii) > (iv) (d) (iv) > (i) > (ii) > (iii)
- Q3. Which of the following is incorrect order of stability  
(a)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} < [\text{AlF}_6]^{3-}$  (b)  $[\text{AlCl}_6]^{3-} < [\text{AlF}_6]^{3-}$   
(c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < [\text{CrF}_6]^{3-}$  (d)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+} < [\text{ZnF}_6]^{4-}$
- Q4. Correct order of stability of complex according to electroneutrality principle is  
(a)  $[\text{Be}(\text{OH}_2)_6]^{2+} > [\text{Be}(\text{OH}_2)_4]^{2+} > [\text{Be}(\text{NH}_3)_4]^{2+}$   
(b)  $[\text{Be}(\text{NH}_3)_4]^{2+} > [\text{Be}(\text{OH}_2)_4]^{2+} > [\text{Be}(\text{OH}_2)_6]^{2+}$   
(c)  $[\text{Be}(\text{OH}_2)_4]^{2+} > [\text{Be}(\text{OH}_2)_6]^{2+} > [\text{Be}(\text{NH}_3)_4]^{2+}$   
(d)  $[\text{Be}(\text{OH}_2)_4]^{2+} > [\text{Be}(\text{NH}_3)_4]^{2+} > [\text{Be}(\text{OH}_2)_6]^{2+}$
- Q5. Arrange the compounds in increasing order of thermodynamic stability:  
(i)  $\text{Al}(\text{NH}_3)_6^{3+}$  (ii)  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  (iii)  $\text{Al}(\text{F}_6)^{3-}$  (iv)  $\text{Mg}(\text{H}_2\text{O})_6^{2+}$   
(a) i > ii > iii > iv (b) iv > iii > ii > i (c) iii > ii > i > iv (d) iii > i > ii > iv
- Q6. Which of the pairs will generally result in tetrahedral coordination complexes, when ligands are  $\text{Cl}^-$  or  $\text{OH}^-$   
(A) Be(II), (Ba)(II) (B) Ba(II), Co(II) (C) Co(II), Zn(II) (D) Be(II), Zn(II)  
(a) A and B (b) B and C (c) C and D (d) A and D
- Q7. Which of the following compound exist  
(a)  $[\text{CoCl}_6]^{4-}$  (b)  $[\text{CoF}_6]^{4-}$  (c)  $[\text{CoBr}_6]^{4-}$  (d)  $[\text{CoI}_6]^{4-}$
- Q8. According to electroneutrality principle the most suitable coordination number for most of the complexes of  $\text{Cu}^{+1}$  is:  
(a) 4 (b) 6 (c) 8 (d) 2

- Q9. Correct statement about  $\text{Ni}(\text{CN})_3^{2-}$  is/are:  
 (a) it doesn't exist (b) it dimerises to give  $\text{Ni}_2(\text{CN})_6^{4-}$   
 (c) it is paramagnetic species (d) coordination number is 2
- Q10. Which of the following can be explained on the basis of electroneutrality principle.  
 (a) Coordination number of transition metal compound.  
 (b) Stability of transition metal compound  
 (c) Stability of Non-transition metal compound  
 (d) All of these
11. The approximate charge on Os in  $\text{OsO}_4$  complex is\_\_\_\_\_.
12. The number of metal ions which can form coordination number 2 complex from the following metal ions  $\text{Cu}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Au}^+$ ,  $\text{Ag}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Ag}^+$ \_\_\_\_\_.
13. Which of the following species is not expected to be a ligand  
 (a)  $\text{NO}^+$  (b)  $\text{NH}_4^+$  (c)  $\text{NH}_2 - \text{N}^+\text{H}_3$  (d) CO
14. Which of the following ligand does not act as bidentate ligand  
 (a) dipy (b) dien (c) gly (d) dmg
15. Pyrazinium ion behave as  
 (a) monodentate (b) Ambidentate  
 (c) Flexidentate (d) No denticity in acidic medium
16. As a ligand  $\text{Cl}^-$   
 (a) Only  $\sigma$ -donor (b) Only  $\pi$ -donor  
 (c) Both  $\sigma$  and  $\pi$ -donor (d) A  $\sigma$ -donor and a  $\pi$ -acceptor
17. Diethylene triamine is:  
 (a) Chelating agent (b) Polydentate ligand  
 (c) Tridentate ligand (d) All of these
18. Among,  $\text{RO}^-$ ,  $\text{AsMe}_3$ ,  $\text{ROR}'$ ,  $\text{CN}^-$ ,  $\text{AsMe}_3$ ,  $\text{RCO}_2^-$ ,  $\text{SCN}^-$ , the set of ligands with good  $\pi$ -acceptor nature are  
 (a)  $\text{RO}^-$ ,  $\text{RCO}_2^-$ ,  $\text{SCN}^-$  (b)  $\text{RO}^-$ ,  $\text{RCO}_2^-$ ,  $\text{AsMe}_3$   
 (c)  $\text{AsMe}_3$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$  (d)  $\text{RO}^-$ ,  $\text{ROR}'$ ,  $\text{RCO}_2^-$
19. Which of the following statements are true about  $\text{NO}_2^-$  ligand.  
 I. Can act as monodentate ligand  
 II. Can act as bidentate ligand  
 III. Act as flexidentate ligand  
 IV. Act as Ambidentate ligand  
 (a) I & II (b) I & IV (c) II & IV (d) I, II, III & IV
20. Which of the following bidentate ligand (s) has similar donor atoms:  
 (a) py (b) bn (c) en (d) gly
21. Which of the following is an example of ambidentate ligand?  
 (a)  $\text{NO}_2^-$  (b)  $\text{CN}^-$  (c)  $\text{OCN}^-$  (d)  $\text{H}^-$
22. Match the list I with list II:  
 (P)  $\text{EDTA}^{4-}$  (1) N – donor atom  
 (Q) en (2) Chelate ligand with same donor site

- (R) gly (3) Bidentate with different donor site  
 (S) amide (4) Hexadentate

**Code:**

	P	Q	R	S
(a)	4	2	1	3
(b)	2	1	3	4
(c)	4	1	2	3
(d)	4	2	3	1

23. Match Column I with Column II :-

**Column I**

**Column II**

(P)  $\pi$ -donor

(i)  $\text{NH}_3$

(Q)  $\pi$ -acceptor

(ii)  $\text{F}^-$

(R) weak  $\pi$ -donor

(iii)  $\text{PR}_3$

(S) No  $\pi$ -effects

(iv)  $\text{H}_2\text{O}$

(a) P-iii, Q - i, R - ii, S-iv (b) P-i, Q -iv , R -iii , S-ii

(c) P-ii, Q -iii , R -iv , S-i (d) P-ii, Q -iii , R -i , S-iv

24. Find the total number of 5-membered rings present in  $[\text{Co}(\text{EDTA})]^-$ .

### ANSWERS

1. (d) 2. (a) 3. (c) 4. (d) 5. (c) 6. (c) 7. (b) 8. (d) 9. (b) 10. (a, c) 11. 1-2 12. 4  
 13. b 14. B 15. A 16. c 17. d 18. c 19. d 20. b, c 21. a, b, c 22. d 23. c

## HINTS AND SOLUTIONS

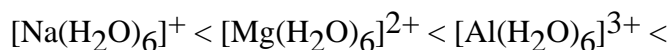
1. (d)

Sol.  $[\text{CoCl}_6]^{4-}$  does not exist on the basis of electroneutrality principle cobalt in +2 oxidation state can form coordination number 4 complex with chloride ligand.  $\text{Co}^{2+}$  can not balance the formal charge due to 6  $\text{Cl}^-$  ligand.

So, correct option is (d)

2. (a)

Sol. Electroneutrality principle can explain the thermodynamic stability of non-transition element. As oxidation state increases stability of complex increases.



So, correct option is (a)

3. (c)

Sol. We cannot explain the thermodynamic stability of transition metal ion on the basis of electroneutrality principle. It depends upon other factors such as CFSE, JTD etc. So,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < [\text{CrF}_6]^{3-}$  is incorrect order of stability.

4. (d)

Sol. In  $[\text{Be}(\text{OH})_2]^{2+}$  &  $[\text{Be}(\text{NH}_3)_4]^{2+}$  electronegativity of oxygen is more than nitrogen. So  $[\text{Be}(\text{OH})_2]^{2+}$  is more stable than  $[\text{Be}(\text{NH}_3)_4]^{2+}$  &  $[\text{Be}(\text{OH}_2)_6]^{2+}$  does not exist as formed charged is not balanced.

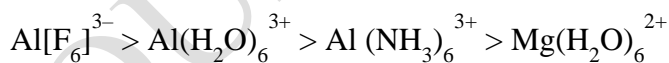
So it does not form CN = 6, it will form CN = 4.

So, correct option is (d)

5. (c)

Sol. According to electroneutrality principle element will more neutralize when most electronegative element combine to form complex. Electronegativity order  $\text{F}^- > \text{OH}_2 > \text{NH}_3$ .

So,  $\text{Al}(\text{F}_6)^{3-} > \text{Al}(\text{H}_2\text{O})_6^{3+} > \text{Al}(\text{NH}_3)_6^{3+}$  and for non transition metal stability will increase when oxidation state increases.



So, correct option is (c)

6. (c)

Sol. For TM ion  $\text{Co}(\text{II})$ ,  $\text{Zn}(\text{II})$  &  $\text{Be}(\text{II})$  form tetrahedral complexes with  $\text{Cl}^-$  &  $\text{OH}^-$ .  $\text{Be}(\text{II})$  has no d-orbitals, therefore, it forms tetrahedral complexes.

So, correct option is (c)

7. (b)

Sol.  $[\text{CoF}_6]^{4-}$  exists because  $\text{F}^-$  is most electronegative element & Co forms CN = 6 when it is combined with most electronegative element of p-acceptor ligand.

Correct option is (b)

8. (d)

Sol. For very low coordination complex (VLCC). CN = 1 to CN = 3 exist for low oxidation state & highest d e Q.

So, CN = 2 is for  $\text{Cu}^+$  ( $d^{10}$ )

9. (b)

Sol. Due to diamagnetic coupling at normal temperature  $\text{Ni}(\text{CN})_3^{2-}$  is dimerises to give  $\text{Ni}_2(\text{CN})_6^{4-}$ .

10. (a, c)

Sol. On the basis of electroneutrality principle we can determine the stability of non-transition metal compound & coordination number of transition metal compound.

11. 1-2

Sol. According to electroneutrality principle real change on a complex exist between +1 to +2.

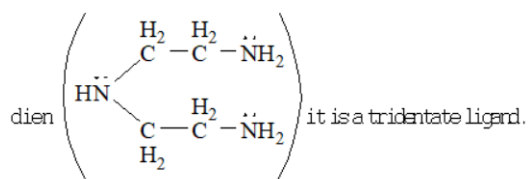
12. 4

Sol. For  $d^{10}$  ion  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Au}^+$ ,  $\text{Hg}^{2+}$  form CN = 2 complex.

13. b

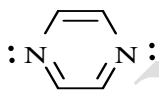
Sol.  $\text{NH}_4^+$  does not expected to be a ligand because ligands are those which can donate atleast one lone pair of electron to metal & in  $\text{NH}_4^+$  it does not have any lone pair of electron.

14. b



Sol:

15. a

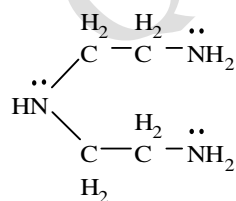
Sol. Pyrazinium  it act as monodentate ligand because it has a single donor atom to bind with metal to form complex.

16. c

Sol.  $\text{Cl}^-$  can act as a both  $\sigma$  as well as  $\pi$ -donor.

17. d

Sol. Diethylene triamine



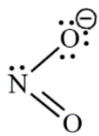
it is tridentate, example of polydentate ligand & also work as chelating ligands because it form ring structure with metal ion.

So, correct option is (d)

18. c

Sol.  $\text{AsMe}_3$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$  act as  $\pi$ -acceptor.  $\text{RO}^-$ , (deprotonated molecules) act as  $\pi$ -donor so all other option  $\text{RO}^-$  is present which act as  $\pi$ -donor, not  $\pi$ -acceptor.

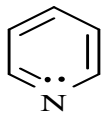
19. d



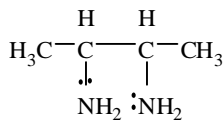
Sol. it act as monodentate, bidentate, flexidentate & ambidentate ligand.

So, correct option is (d)

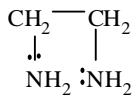
20. b, c



Sol. py  $\rightarrow$  it is monodentate ligand,



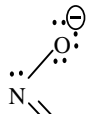
bn  $\rightarrow$  it act as bidentate ligand



en  $\rightarrow$  it act as bidentate ligand

gly  $\rightarrow \text{NH}_2 - \text{CH}_2 - \text{COO}^-$  it act as bidentate ligand but different donor atom.

21. a, b, c



Sol.  $\text{O}^-$ ,  $\text{C} \equiv \text{N}$ , are ambidentate ligand.  $\text{H}^-$  is not ambidentate ligand because it does not having different donor amount.

22. d

Sol: EDTA<sup>4-</sup>  $\rightarrow$  Hexadentate  
 en  $\rightarrow$  Chelate ligand with same donor site  
 gly  $\rightarrow$  Bidentate with different donor site  
 amide  $\rightarrow$  N – donor atom

23. c

Sol.  $\pi$ -donor  $\rightarrow \text{F}^-$   
 $\pi$ -acceptor  $\rightarrow \text{PR}_3$   
 weak  $\pi$ -donor  $\rightarrow \text{H}_2\text{O}$   
 No  $\pi$ -effects  $\rightarrow \text{NH}_3$

So, correct option is (c)

• • • • •



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

---

## DPP-5 COORDINATION

---

- Q1. According to Kepert model which of the following possesses least common geometries with coordination number 6.
- (a) Octahedral (b) Trigonal prismatic  
(c) Octahedral and trigonal prismatic both (d) None of the above
- Q2. What is the geometry of  $[Y\{N(SiMe_3)_2\}_3]$  in solid state and  $[Fe\{N(SiMe_3)_2\}_3]$
- (a) trigonal pyramidal, trigonal planar respectively  
(b) trigonal planar, trigonal planar  
(c) trigonal pyramidal, trigonal pyramidal  
(d) trigonal planar, trigonal pyramidal respectively.
- Q3. What is coordination number of Cu(I) in (i)  $[Cu(CN)_3]^{2-}$  (ii)  $[Cu(CN)_2]^-$
- (a) 3, 3 (b) 2, 3 (c) 2, 2 (d) 3, 2
- Q4. What is coordination number of Hg(II) in  $[HgI_3]^-$  and  $[Hg(SPh)_3]^-$
- (a) 3, 3 (b) 2, 3 (c) 2, 2 (d) 3, 2
- Q5. What is the correct order of bond angle in the following complexes.
- (a)  $Cu(NH_3)_2^+ = Cu(PH_3)_2^+ = Cu(CO)_2^+$   
(b)  $Cu(NH_3)_2^+ > Cu(PH_3)_2^+ > Cu(CO)_2^+$   
(c)  $Cu(NH_3)_2^+ < Cu(PH_3)_2^+ < Cu(CO)_2^+$   
(a)  $Cu(NH_3)_2^+ > Cu(PH_3)_2^+ = Cu(CO)_2^+$
- Q6. Which amongst the following are organometallic compounds?
- (i)  $Al_2(CH_3)_6$  (ii)  $K[PtCl_3C_2H_5]$  (iii)  $N(CH_3)_3$
- (a) (i) only (b) (iii) only (c) (i), (ii) (d) (i), (ii) & (iii)
- Q7. Which of the following statements are true.
- (a) Steric and electronic factors determine the coordination geometry around the metal centre.  
(b) The structures of d-block complexes vary when the number of electrons around the metal center changes.  
(c) The size of metal ion decreases as the formal charge increases, e.g.  $r(Fe^{3+}) < r(Fe^{2+})$   
(d) Using VSEPR model we can predict the shape of coordination compounds.
- Q8. Which of the following statements are true.
- (a)  $[ML_n]$ ,  $[ML_n]^{m+}$  and  $[ML_n]^{m-}$  have the same coordination geometry  
(b)  $[Cu(CN)_3]^{2-}$  is predicted to be trigonal pyramidal  
(c) The four nitrogen donor atoms of a porphyrin ligand are confined to a square planar array.



- (d) Tripodal ligands have limited flexibility and are not always free to adopt position predicted by keper.
- Q9. Which of the following statements are true.
- In same oxidation state the coordination number increase with increase in no. of d electrons
  - Generally in transition metal ion in high oxidation state complex form high coordination number complexes.
  - Sigma donor ligand prefer to bind with electron deficient metal center
  - A tripodal ligand is one containing three arms, each with a donor atom, which stem from a central atom or group.
- Q10. Which of the pair will generally result in tetrahedral coordination complexes, when ligands are  $\text{Cl}^-$  or  $\text{OH}^-$
- $\text{Ba(II)}$ ,  $\text{Co(II)}$
  - $\text{Be(II)}$ ,  $\text{Ni(II)}$
  - $\text{Cu(II)}$ ,  $\text{Zn(II)}$
  - $\text{Ni(II)}$ ,  $\text{Zn(II)}$
- Q11. Which of the following statements are true.
- Bulky ligands often result in low coordination numbers
  - High coordination numbers are most common when the metal ions have larger radii.
  - Generally compound of coordination number 2 have  $C_{\infty v}$  symmetry.
- Q12. How many from the following complex are stable.  
 $[\text{Ni}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]^{2+}$ ,  $[\text{Ni}(\text{NH}_3)_4]$ ,  $[\text{Ni}(\text{CN})_4]^{4-}$ ,  $[\text{Ni}(\text{CO})_4]$
- Q13. How many from the following do not exist.  
 $[\text{NiCl}_6]^{4-}$ ,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]^{2+}$ ,  $[\text{NiF}_6]^{4-}$ ,  $\text{HgCl}_2$
- Q14. How many metal centre from the following does not have linear environment.  
 $[\text{CuCl}_2]^-$ ,  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{Au}(\text{CN})_2]^-$ ,  $(\text{R}_3\text{P})-\text{AuCl}$ ,  $[\text{Au}(\text{PR}_3)_2]^+$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{K}[\text{Cu}(\text{CN})_2]$ ,  $[\text{Fe}\{\text{N}(\text{SiMePh}_2)_2\}]$ ,  $[\text{Cu}(\text{CN})_2]^-$
- Q15. What is coordination number of Cu in  $\text{CuCN}$
- Q16. What is coordination number of Pt in  $[\text{Pt}(\text{Pcy}_3)_3]$  complex?
- Q17. What is the coordination number of Cu in cyclic compound  $[\text{Cu}(\text{SPMe}_3)\text{Cl}]_3$ .
- Q18. How many from the following have linear arrangement  $\text{Au}(\text{CO})_2^+$ ,  $\text{Au}(\text{PH}_3)_2^+$ ,  $\text{Au}(\text{NH}_3)_2^+$ ,  $\text{Rh}(\text{NH}_3)_2^-$ ,  $\text{Rh}(\text{PH}_3)_2^-$ ,  $\text{Rh}(\text{CO})_2^-$ .
- Q19. What is the numbers of unpaired electrons in  $[\text{AuCl}_2]^-$ ,  $[\text{Cu}(\text{CN})_2]^-$  and  $[\text{Ag}(\text{NH}_3)_2]^+$  complexes.

## ANSWERS

- |            |         |         |         |         |         |           |              |              |               |
|------------|---------|---------|---------|---------|---------|-----------|--------------|--------------|---------------|
| 1. (b)     | 2. (a)  | 3. (a)  | 4. (a)  | 5. (a)  | 6. (c)  | 7. (a, c) | 8. (a, c, d) | 9. (b, c, d) | 10. (b, c, d) |
| 11. (a, b) | 12. (4) | 13. (2) | 14. (3) | 15. (2) | 16. (3) | 17. (3)   | 18. (4)      | 19. (0)      |               |

## HINTS AND SOLUTIONS

1. (b)

Sol. Trigonal prismatic is least common geometries with coordination number 6.

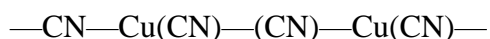
2. (a)

Sol.  $[Y\{N(SiMe_3)_2\}_3]$  in solid state have trigonal pyramidal geometry and  $[Fe\{N(SiMe_3)_2\}_3]$  have trigonal planar geometry.

3. (a)

Sol. The  $Cu(CN)_3^{2-}$  anion has trigonal planar structure and the coordination number of Cu(I) is (3).

$[Cu(CN)_2]^-$  structure instead of the expected discrete, linear complex ion, there exist polymer of composition  $[Cu(CN)_2]_{\infty}^-$ . These polymers are in the form of chains spiralling around a two fold screw axis and Cu(I) atom has been shown to have three fold coordination.



4. a

Sol. Coordination number of Hg(II) in  $[HgI_3]^-$  and  $[Hg(SPh_3)_3]^-$  is 3.

5. a

Sol. Complexes  $Cu(NH_3)_2^+$ ,  $Cu(PH_3)_2^+$  and  $Cu(CO)_2^+$  all have linear arrangement and bond angle is  $180^\circ$ .

6. c

Sol.  $Al_2(CH_3)_6$  and  $K[PtCl_3C_2H_2]$  are organometallic compounds.

7. Correct answer is (a, c).

Sol. According to VSEPR model steric and electronic factors determine the coordination geometry around the metal center. Due to increase in formal positive charge size of metal ion decreases.

8. Correct answer is (a, c, d).

Sol. According to VSEPR model  $[ML_n]$ ,  $[ML_n]^{m+}$  and  $[ML_n]^{m-}$  have same geometry. For example if  $n = 6$  then it will form octahedral complex irrespective of charge on metal ion. The four nitrogen donor atom in porphyrin are rigid and are confined to a square planar array. Tripodal ligands are attached to a single atom so, their arms are not flexible.

9. Correct answer is (b, c, d).

Sol. As the oxidation state by metal increases high coordination number complexes are favourable. Sigma donor ligands prefer to bind with electron deficient centre and acceptor bind with electron rich centre. A tripodal ligand have three arms attached to single central atom.

10. Correct answer is (b, c, d).

Sol. Metal ion Be(II), Ni(II), Cu(II), Zn(II) form tetrahedral coordination complex when ligands are  $Cl^-$  or  $OH^-$ .

11. a, b

Sol. Bulky ligands results in low coordination number due to steric factor. When metal ion have large radii then high coordination numbers are commonly observed.

Linear compound have  $D_{\infty h}$  symmetry so, correct answer is (a) & (b).

12. (4)

Sol. According to electroneutrality principle  $[\text{Ni}(\text{NH}_3)]^{2+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Ni}(\text{CN})_4]^{4+}$  are stable.

13. (2)

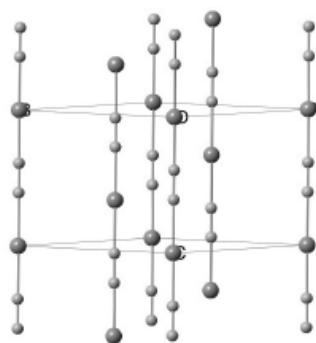
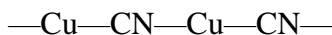
Sol.  $[\text{NiCl}_6]^{4-}$  and  $[\text{Ni}(\text{CO})_4]^{2+}$  does not exist.

14. (3)

Sol.  $\text{K}[\text{Cu}(\text{CN})_2]$  is coordination number 3 complex and  $[\text{Fe}\{\text{N}(\text{SiMePh}_2)_2\}_2]$  and  $[\text{Cu}(\text{CN})_2]^-$  does not have linear arrangement.

15. 2

Sol. It exist in a linear chain structure



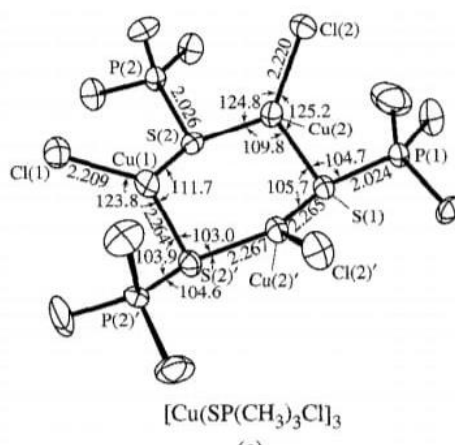
So, coordination number is (2).

16. 3

Sol. Coordination number of Pt in  $[\text{Pt}(\text{Pcy}_3)_3]$  complex is 3.

17. 3

Sol. Coordination number of Cu in cyclic compound  $[\text{Cu}(\text{SPMe}_3)\text{Cl}]_3$  is 3 as shown in figure.



18. 4

Sol. Complex  $\text{Au}(\text{CO})_2^+$ ,  $\text{Au}(\text{PPh}_3)_2^+$ ,  $\text{Au}(\text{NH}_3)_2^+$  and  $\text{Rh}(\text{NH}_3)_2^-$  have linear arrangement and  $\text{L—M—L}$  bond angle in  $\text{Rh}(\text{PH}_3)_2^-$  is 141.2 and for  $\text{Rh}(\text{CO})_2^-$  is 130.8

19. 0

Sol. The complexes  $[\text{AuCl}_2]^-$ ,  $[\text{Cu}(\text{CN})_2]^-$  and  $[\text{Ag}(\text{NH}_3)_2]^+$  all have  $d^{10}$  configuration and number of unpaired electrons is zero.

• • • • •



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

---

## DPP-6 COORDINATION

---

- Which of the following has lowest oxidation state of central atom?  
(a)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]$  (b)  $\text{Na}[\text{Co}(\text{CO})_4]$  (c)  $\text{Fe}(\text{CO})_5$  (d)  $[\text{Co}(\text{en})_3]\text{Cl}_3$
- On the basis of magnetic moment data the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is found to be diamagnetic what can you say about the hybridisation of complex.  
(a)  $\text{sp}^3\text{d}^2$  (b)  $\text{d}^2\text{sp}^3$  (c)  $\text{p}^3\text{d}^3$  (d)  $\text{pd}^5$
- $\text{K}_2[\text{NiF}_6]$  is diamagnetic while  $\text{K}_3[\text{CoF}_6]$  is paramagnetic what can you say about the hybridisation of complex.  
(a)  $\text{d}^2\text{sp}^3$ ,  $\text{d}^2\text{sp}^3$  (b)  $\text{sp}^3\text{d}^2$ ,  $\text{sp}^3\text{d}^2$  (c)  $\text{sp}^3\text{d}^2$ ,  $\text{d}^2\text{sp}^3$  (d)  $\text{d}^2\text{sp}^3$ ,  $\text{sp}^3\text{d}^2$
- What is the geometry and point group of complex  $[\text{ZrMe}_6]^{2-}$ .  
(a) Octahedral,  $\text{Oh}$  (b) distorted octahedral  $\text{C}_{3v}$   
(c) Trigonal prismatic,  $\text{D}_{3h}$  (d) distorted trigonal prismatic,  $\text{C}_{3v}$
- What is the geometry and point group of complex  $[\text{TaPh}_6]^-$ .  
(a) Octahedral,  $\text{Oh}$  (b) distorted octahedral  $\text{C}_{3v}$   
(c) Trigonal prismatic,  $\text{D}_{3h}$  (d) distorted trigonal prismatic,  $\text{C}_{3v}$
- What can you say about the geometry of complex  $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$  and  $[\text{Re}(\text{S}_2\text{C}_2\text{PH}_2)_3]$   
(a) Octahedral, Octahedral (b) Octahedral, trigonal Prismatic  
(c) Trigonal Prismatic, Octahedral (d) Trigonal Prismatic, Trigonal Prismatic
- Among the following ions, which have the highest paramagnetism?  
(a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- In which of the following complexes the nickel metal is in highest oxidation state.  
(a)  $\text{Ni}(\text{CO})_4$  (b)  $\text{K}_2\text{NiF}_6$   
(c)  $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2$  (d)  $\text{K}_4[\text{Ni}(\text{CN})_6]$
- In nitroprusside ion the iron and NO exist as  $\text{Fe}^{2+}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{3+}$  and NO. These forms can be differentiated by  
(a) estimating the concentration of iron (b) measuring the concentration of  $\text{CN}^-$   
(c) measuring state magnetic moment (d) thermally decomposing the compound
- $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$  have similarity but not in  
(a) Magnetic moment (b) Coordination number  
(c) Structure (d) Both in (a) and (c)
- Which of the following is true for  $[\text{Ni}(\text{en})_2]^{2+}$   
(a) Paramagnetic,  $\text{dsp}^2$ , square planar, C. N. of Ni = 2  
(b) Diamagnetic  $\text{dsp}^2$ , square planar, C. N. of Ni = 4

- (c) Diamagnetic,  $sp^3$ , tetrahedral, C. N. of Ni = 4  
 (d) Paramagnetic,  $sp^3$ , square planar, C. N. of Ni = 4
12. Among  $Ni(CO)_4$ ,  $[Ni(CN)_4]^{2-}$  and  $[NiCl_4]^{2-}$   
 (a)  $Ni(CO)_4$  and  $[Ni(CN)_4]^{2-}$  are diamagnetic and  $NiCl_4^{2-}$  is paramagnetic  
 (b)  $Ni(CO)_4$  and  $NiCl_4^{2-}$  are diamagnetic and  $Ni(CN)_4^{2-}$  is paramagnetic  
 (c)  $Ni(CO)_4$  is diamagnetic and  $[Ni(CN)_4]^{2-}$  and  $NiCl_4^{2-}$  are paramagnetic  
 (d)  $NiCl_4^{2-}$  and  $[Ni(CN)_4]^{2-}$  are diamagnetic and  $Ni(CO)_4$  is paramagnetic
13. The structure of the complexes  $[Cu(NH_3)_4](ClO_4)_2$  and  $[Cu(NH_3)_4]ClO_4$  in the solution respectively are:-  
 (a) Square planar and tetrahedral (b) Octahedral and square pyramidal  
 (c) Octahedral and trigonal bipyramidal (d) Tetrahedral and square planar
14. The complex  $[Pt(CN)_4]^{2-}$  and  $[NiCl_4]^{2-}$  respectively are:  
 (a) Paramagnetic, paramagnetic (b) Diamagnetic, diamagnetic  
 (c) Paramagnetic, paramagnetic (d) Diamagnetic, paramagnetic
15. Out of  $[Fe(CN)_6]^{4-}$ ,  $[Ni(CN)_4]^{2-}$  and  $[Ni(CO)_4]$   
 (a) All have identical geometry (b) All are paramagnetic  
 (c) All are diamagnetic  
 (d)  $[Fe(CN)_6]^{4-}$  is diamagnetic but  $[Ni(CN)_4]^{2-}$  and  $[Ni(CO)_4]$  are paramagnetic

---

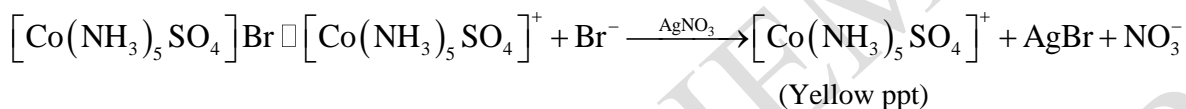
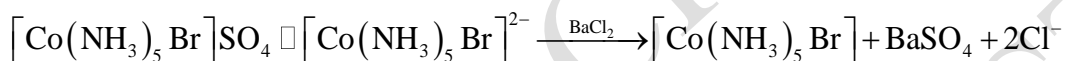
**ANSWERS**


---

1. (b) 2. (b) 3. (d) 4. (c) 5. (d) 6. (d) 7. (b) 8. (b) 9. (c) 10. (d) 11. (b) 12. (a) 13. (a) 14. (d)  
 15. (c)

## HINTS AND SOLUTIONS

1. ()

Sol. Red compound is  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ It ionises to give  $\text{Br}^-$  ions in the solution and therefore, form yellow ppt, of  $\text{AgBr}$  with  $\text{AgNO}_3$  solution.Violet compound is  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ . It ionises to give  $\text{SO}_4^{2-}$  ions which gives white ppt with  $\text{BaCl}_2$  solution.

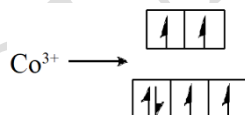
2. (b)

Sol.  $[\text{Fe}(\text{CN})_6]^{3-}$  O.N. = +3 $\text{Na}[\text{Co}(\text{CO})_4]$  O.N. = -1 $\text{Fe}(\text{CO})_5$  O.N. = 0 $[\text{Co}(\text{en})_3]\text{Cl}_3$  O.N. = +3

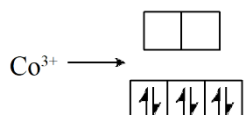
Correct option is (b)

3. (b)

Sol. In case of high spin complex

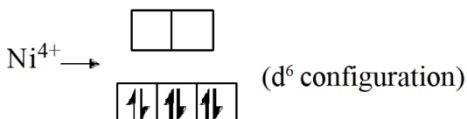
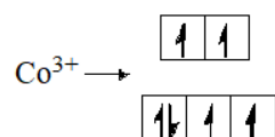
 $n = 4$ , So, it is paramagnetic

In case of low spin complex

 $n = 0$ , So, it diamagnetic and hybridisation will be  $d^2sp^3$ .

So, correct option is (b)

4. (d)

Sol.  $\text{K}_2[\text{NiF}_6]$  here Ni is present is +4 oxidation state and is diamagnetic in nature.So, hybridisation is  $d^2sp^3$  $\text{K}_3(\text{CoF}_6)$  $\text{Co}^{3+}$  ( $d^6$ ) is paramagnetic in natureSo, will form outer orbital complex and hybridisation will be  $sp^3d^2$ 

5. (c)

- Sol.  $[\text{ZrMe}_6]^{2-}$  with  $d^6$  electronic configuration has regular trigonal prismatic geometry and point group is  $D_{3h}$ .
6. (d)
- Sol.  $[\text{TaPh}_6]^-$  with  $d^6$  electronic configuration has distorted trigonal prism geometry and point group is  $C_{3v}$ .
7. (d)
- Sol. Both the complexes  $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$  and  $[\text{Re}(\text{S}_2\text{C}_2\text{PH}_2)_3]$  have trigonal prismatic geometry.
8. (b)
- Sol.  $\text{Cr}^{3+}$  ( $d^3$ ) has 3 unpaired electron and is paramagnetic  $\text{Fe}^{3+} (t_{2g}^3 e_g^2)$  has 5 unpaired electron and is paramagnetic  
 $\text{Fe}^{2+} (t_{2g}^4 e_g^2)$  has 4 unpaired electron and is paramagnetic  
 $\text{Cu}^{2+} (t_{2g}^6 e_g^3)$  has 1 unpaired electron and is paramagnetic
9. (b)
- Sol.  $\text{K}_2\text{NiF}_6$   
 $\text{NiF}_6^{2-}$  here oxidation state of Ni is +4.
10. (c)
- Sol. These form can be differentiated by measuring the magnetic moment.
11. (d)
- Sol.  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$  both are coordination number 4 complex.  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar and  $[\text{NiCl}_4]^{2-}$  is tetrahedral and magnetic moment is also different.
12. (b)
- Sol.  $[\text{Ni}(\text{en})_2]^{2+}$  is coordination number = 2 complex and will have square planar geometry ( $dsp^2$ ) and diamagnetic in nature.
13. (a)
- Sol.  $\text{Ni}(\text{CO})_4$  has  $d^{10}$  configuration and is diamagnetic in nature. In  $[\text{Ni}(\text{CN})_4]^{2-}$  complex  $\text{CN}^-$  behave as strong field ligand and electron get paired, is therefore diamagnetic in nature.  $[\text{NiCl}_4]^{2-}$  will form tetrahedral complex and will have two unpaired electron therefore paramagnetic.
14. ()
15. (a)
- Sol. In  $[\text{Cu}(\text{NH}_3)_4](\text{ClO}_4)_2$  complex oxidation state of Cu is +2 and  $\text{NH}_3$  will behave as strong field ligand therefore geometry will be square planar.  
 In  $[\text{Cu}(\text{NH}_3)_4]\text{ClO}_4$  complex oxidation state of Cu is +1 and has  $d^{10}$  configuration and therefore tetrahedral geometry.

• • • • •



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (7)

- Which of the following theory is based on purely electrostatic interaction between the ligands and the metal ion—  
(a) Werner's theory (b) Crystal field theory  
(c) Ligand field theory (d) Valance bond theory
- In presence of a spherically symmetrical field of negative charges around metal, what is observed—  
(a) orbitals remains degenerate but their energy is raised  
(b) orbitals remains degenerate and no effect on their energy  
(c) splitting of orbitals takes place  
(d) only energy of orbitals is lowered.
- When six ligand approach the metal center to form octahedral complex, which orbitals experience greater repulsion—  
(a) Non-axial d-orbitals (b) axial d-orbitals  
(c) all orbitals experience equal repulsions (d) none of above
- In presence of field effects, which of the following orbitals don't undergo splitting—  
(a) p and d orbitals (b) s and p orbitals (c) d and f orbitals (d) s and d orbitals
- The correct order of energy levels for octahedral complexes—  
(a)  $e_g > t_{2g} < d_{(ES)} < d_{(GS)}$  (b)  $e_{2g} > e_g > d_{(ES)} > d_{(GS)}$   
(c)  $e_g > d_{(ES)} > t_{2g} > d_{(GS)}$  (d)  $d_{(ES)} > e_g < t_{2g} < d_{(GS)}$
- The magnitude of splitting is correctly represented in which of the following  
(a)  $\Delta_{sp} > \Delta_o > \Delta_c > \Delta_t$  (b)  $\Delta_o > \Delta_{sp} > \Delta_c > \Delta_t$   
(c)  $\Delta_{sp} > \Delta_c > \Delta_o > \Delta_t$  (d)  $\Delta_c > \Delta_o > \Delta_{sp} > \Delta_t$
- The d-orbitals involved in the hybridization to form square planar and trigonal bipyramidal geometry are, respectively—  
(a)  $d_{z^2}$  &  $d_{z^2}$  (b)  $d_{yx}$  &  $d_{z^2}$  (c)  $d_{x^2-y^2}$  &  $d_{z^2}$  (d)  $d_{x^2-y^2}$  &  $d_{yz}$



8. The correct order of d-orbital splitting for  $[\text{AuCl}_4]^\ominus$ —
- (a)  $d_{x^2-y^2} > d_{xy} > d_{z^2} > (d_{xz} = d_{yz})$  (b)  $d_{x^2-y^2} > d_{z^2} > d_{xy} > (d_{xz} = d_{yz})$   
 (c)  $(d_{x^2-y^2} = d_{z^2}) > (d_{xy} = d_{yz} = d_{xz})$  (d)  $(d_{xy} = d_{yz} = d_{xz}) > (d_{x^2-y^2} = d_{z^2})$
9. Among the following options, which is correct for  $\text{SbPh}_5$  geometry and highest energy orbital, respectively—
- (a) Trigonal bipyramidal,  $d_{z^2}$  (b) Square pyramidal  $d_{x^2-y^2}$   
 (c) Trigonal bipyramidal,  $d_{xy}$  (d) Square pyramidal,  $d_{z^2}$
10. In the trigonal bipyramidal crystal field, the d-orbital with the highest energy is—
- (a)  $d_{xy}$  (b)  $d_{x^2-y^2}$  (c)  $d_{yz}$  (d)  $d_{z^2}$
11. According to the crystal field theory,  $\text{Ni}^{2+}$  can have two unpaired electrons in—
- (a) Octahedral geometry only (b) Square planar geometry only  
 (c) tetrahedral geometry only (d) Both octahedral and tetrahedral geometry
12. The correct order of d-splitting in a trigonal bipyramidal geometry is:
- (a)  $d_{z^2} > d_{xz} > d_{x^2-y^2}, d_{xy}$  (b)  $d_{xz}, d_{yz} > d_{x^2-y^2}, d_{xy} > d_{z^2}$   
 (c)  $d_{x^2-y^2}, d_{xy} > d_{z^2} > d_{xz}, d_{yz}$  (d)  $d_{z^2} > d_{x^2-y^2}, d_{xy} > d_{xz}, d_{yz}$
13. In trigonal prismatic ligand field, the most stabilized d-orbital is—
- (a)  $d_{xy}$  (b)  $d_{xz}$  (c)  $d_{yz}$  (d)  $d_{z^2}$
14. For the complex  $\text{Fe}(\text{CO})_5$ , the correct combination of geometry and most destabilized d-orbital is—
- (a) trigonal bipyramidal,  $d_{z^2}$  (b) trigonal bipyramidal,  $d_{x^2-y^2}$   
 (c) square pyramidal  $d_{z^2}$  (d) square pyramidal,  $d_{x^2-y^2}$
15. The correct order of d-orbital splitting in a square antiprismatic geometry—
- (a)  $(d_{xz} = d_{yz}) > (d_{xy} = d_{x^2-y^2}) > d_{z^2}$  (b)  $(d_{xz} = d_{yz}) > d_{z^2} > (d_{xy} = d_{x^2-y^2})$   
 (c)  $(d_{xy} = d_{x^2-y^2}) > (d_{xz} = d_{yz}) > d_{z^2}$  (d)  $d_{x^2-y^2} > d_{xy} > (d_{xz} = d_{yz}) > d_{z^2}$
16. The highest energy d-orbital for dodecahedral geometry is—
- (a)  $d_{x^2-y^2}$  (b)  $d_{xz}$  (c)  $d_{z^2}$  (d)  $d_{xy}$
17. For the given complexes—
- (A)  $[\text{Ni}(\text{CO})_4]$  (B)  $[\text{Ni}(\text{CN})_4]^{2-}$
- The correct statement is/are—
- (a) A is tetrahedral and B is a square planar (b) Higher energy state for A is doubly degenerate  
 (c) Highest energy d-orbital for B is  $d_{x^2-y^2}$  (d) Higher energy state of A is triply degenerate

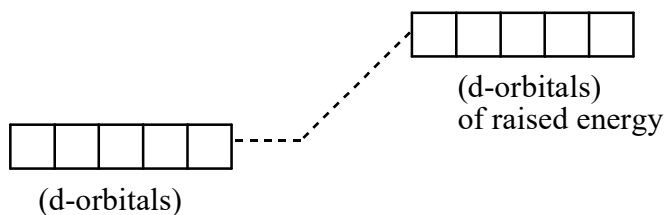
18. The incorrect statement among the following is—
- $\text{NiF}_6^{2-}$ ,  $(d_{x^2-y^2} = d_{z^2}) > (d_{yz} = d_{yz} = d_{zx})$
  - $[\text{ZnCl}_4]^{2-}$ ,  $(d_{xz} = d_{yz} = d_{zx}) < (d_{x^2-y^2} = d_{z^2})$
  - $[\text{CuCl}_5]^{3-}$ ,  $d_{z^2} > (d_{xy} = d_{x^2-y^2}) > (d_{xz} = d_{yz})$
  - $\text{Ni}(\text{CO})_4$ ,  $(d_{x^2-y^2} = d_{z^2}) > (d_{xy} = d_{yz} = d_{zx})$
19. Which of the following geometries have doubly degenerate highest energy state—
- Octahedral
  - Triagonal prismatic
  - Square antiprismatic
  - pentagonal antiprismatic
20. The correct statements regarding crystal field theory—
- accounted satisfactorily for relative strength of ligands
  - didnot considered covalent character in transition metal complexes
  - gave no consideration to any other orbitals apart from d-orbitals
  - interactions between metal and ligands was purely electrostatic.

### ANSWER KEY

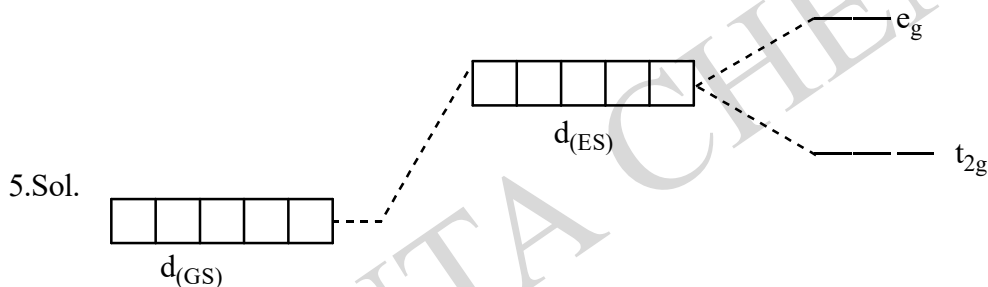
- |         |         |             |           |               |             |         |
|---------|---------|-------------|-----------|---------------|-------------|---------|
| 1. (b)  | 2. (a)  | 3. (b)      | 4. (b)    | 5. (c)        | 6. (a)      | 7. (c)  |
| 8. (a)  | 9. (b)  | 10. (d)     | 11. (d)   | 12. (d)       | 13. (d)     | 14. (a) |
| 15. (a) | 16. (d) | 17. (a,c,d) | 18. (b,d) | 19. (a,b,c,d) | 20. (b,c,d) |         |

## HINTS & SOLUTION

- 1Sol. Crystal field theory is based upon purely electrostatic interaction between ligand and metal ion.
- 2Sol. Whenever a spherically symmetrical field of negative charges are present around metal, the d-orbitals of metal will remain degenerate but their energy will be raised.



- 3Sol. The orbitals lying along the axes ( $d_{z^2}$  &  $d_{x^2-y^2}$ ) will be more strongly repelled than the orbitals with lobes directed between the axes ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ).
- 4Sol. In presence of field effects, p orbitals get raised in energy and s orbitals remains intact. None of them undergo splitting.



- 5Sol.
- $$\therefore e_g > d_{(ES)} > t_{2g} > d_{(GS)}$$

6Sol.  $\Delta_t = \frac{4}{9} \Delta_o$

$$\Delta_c = \frac{8}{9} \Delta_o$$

$$\Delta_{sp} = 1.3\Delta_o \text{ to } 2\Delta_o$$

$$\therefore \Delta_{sp} > \Delta_o > \Delta_c > \Delta_t$$

- 7Sol. The d-orbitals involved are according to symmetry match with other orbitals involved in hybridization.

Square planar is z-excluded geometry, so  $d_{x^2-y^2}$  orbital is involved

In TBP,  $d_{z^2}$  orbital is involved because TBP is a combination of  $(s + p_x + p_y)$  and  $(p_z + d_{z^2})$

- 8Sol.  $[\text{AuCl}_4]^\ominus \Rightarrow \text{Au}^{3+} \Rightarrow 5d^8 \text{ configuration} \Rightarrow \text{all ligands will act as SFL}$

$\therefore$  Square planar complex  $\rightarrow dsp^2$

Energy splitting diagram for square planar complexes—

$$d_{x^2-y^2} > d_{xy} > d_{z^2} > (d_{xy} = d_{yz})$$

- 9Sol.  $\text{SbPh}_3$  is square pyramidal

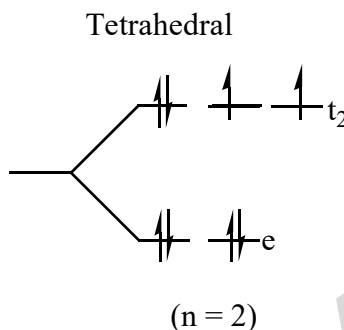
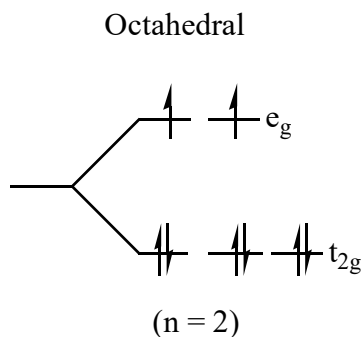
Energy of d-orbitals for square pyramidal geometry is–

$$d_{x^2-y^2} > d_{z^2} > d_{xy} > (d_{xz} = d_{yz})$$

10.Sol. For TBP crystal field;

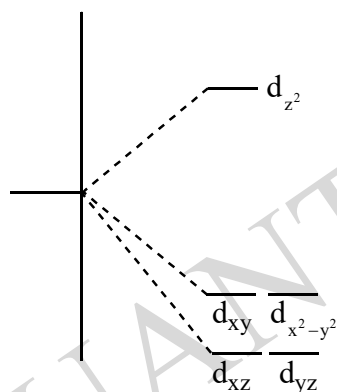
$$d_{z^2} > (d_{xy} = d_{x^2-y^2}) > (d_{xz} = d_{yz})$$

11.Sol. In case of  $N^{2+} \Rightarrow 3d^8$

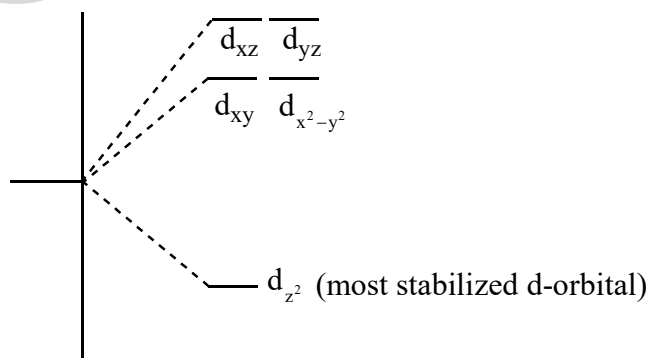


In case of square planar geometry, no. of unpaired electrons,  $n = 0$ .

12.Sol.



13.Sol. Splitting diagram of d-orbitals in trigonal prismatic ligand field–

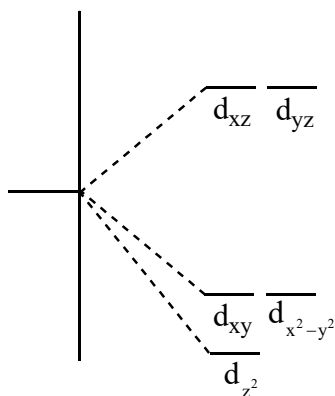


14.Sol.  $Fe(CO)_5$  has trigonal bipyramidal geometry and the energy order of d-orbitals is as follows–

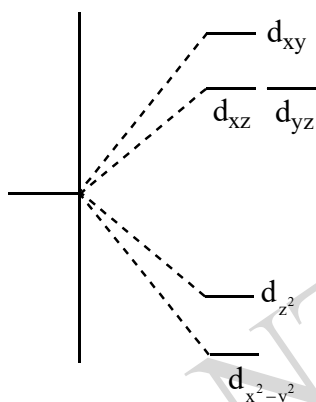
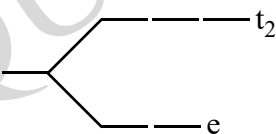
$$d_{z^2} > d_{xy} = d_{x^2-y^2} > d_{xz} = d_{yz}$$

15.Sol. Square antiprismatic geometry

splitting energy diagram—



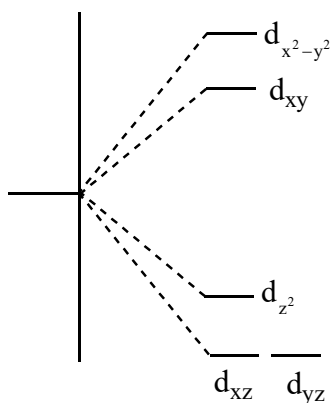
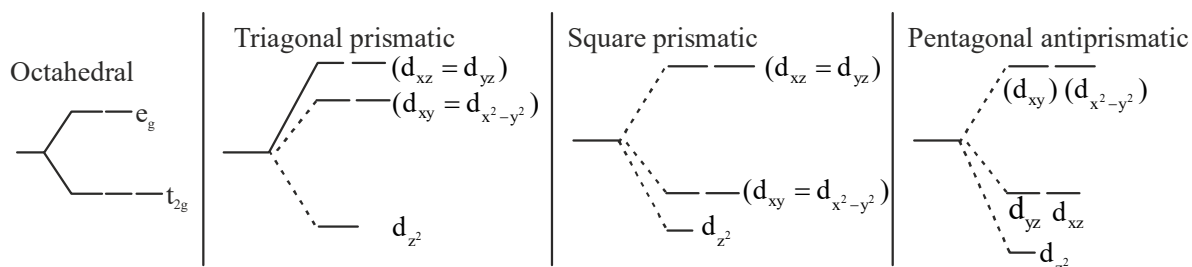
16.Sol. Dodecahedral splitting energy diagram—

17.Sol.  $\text{Ni}(\text{CO})_4 \Rightarrow \text{Ni} \Rightarrow 3d^8 4s^2 \Rightarrow d^{10}$  (converted system)Higher energy state  $\Rightarrow t_2 \Rightarrow$  triply degenerate $[\text{Ni}(\text{CN})_4]^{2-} \Rightarrow \text{Ni}^{2+} \Rightarrow 3d^8$  in presence of SFL

• Square planar geometry

18. Sol.  $[\text{ZnCl}_4]^{2-} \Rightarrow \text{Zn}^{2+} \Rightarrow 3d^{10} \Rightarrow$  tetrahedral geometryEnergy of orbitals  $\Rightarrow (d_{x^2-y^2} = d_{z^2}) < (d_{xz} = d_{yz} = d_{zx})$  $\text{Ni}(\text{CO})_4 \Rightarrow 3d^8 4s^2 \Rightarrow d^{10}$  (converted system)energy of orbitals  $\Rightarrow (d_{x^2-y^2} = d_{z^2}) < (d_{xz} = d_{yz} = d_{zx})$ 

19. Sol. Splitting diagrams for—



- Higher energy state  $\Rightarrow d_{x^2-y^2}$

20. Sol. According to crystal field theory (CFT)

- the interaction between metal & ligand is purely electrostatic
- no consideration of covalent character in any complex
- only considered d-orbitals in interactions



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (8)

- Arrange the following in increasing order of splitting energy:  
(i)  $\text{CoCl}_6^{3-}$       (ii)  $[\text{Co}(\text{CN})_6]^{3-}$       (iii)  $[\text{IrCl}_6]^{3-}$   
(a) (i) < (ii) < (iii)      (b) (i) < (iii) < (ii)      (c) (i) > (ii) > (iii)      (d) None
- Which of the following correctly places the metal centres in the spectrochemical series?  
(a)  $\text{Br}^- < \text{Cl}^- < \text{NH}_3 < \text{H}_2\text{O}$       (b)  $\text{I}^- < \text{Br}^- < \text{H}_2\text{O} < \text{OH}^-$   
(c)  $\text{F}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3$       (d)  $\text{I}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{en}$
- The octahedral crystal field splitting ( $\Delta_o$ ) of d orbital energies of the following metal ions decreases in the order  
(a)  $\text{Co}^{2+} > \text{Co}^{3+} > \text{Rh}^{3+}$       (b)  $\text{Rh}^{3+} > \text{Co}^{3+} > \text{Co}^{2+}$   
(c)  $\text{Rh}^{3+} > \text{Co}^{2+} > \text{Co}^{3+}$       (d)  $\text{Co}^{3+} > \text{Co}^{2+} > \text{Rh}^{3+}$
- The  $\text{FeX}_6^{3+}$ , where X is a monodentate ligand, has one unpaired electron. The X ligand produces a  
(a) weak field      (b) strong field      (c) strong & weak field  
(d) none of these
- Among the following which one has highest value of  $\Delta_o$ .  
(a)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       (b)  $[\text{Ir}(\text{NH}_3)_6]^{3+}$       (c)  $[\text{Fe}(\text{bpy})_3]^{3+}$       (d)  $[\text{Fe}(\text{NH}_3)_6]^{2+}$
- The increasing order of crystal field splitting ( $\Delta_o$ ) for a given metal ion:  
(a)  $\text{C}_2\text{H}_5\text{OH} < \text{Cl}^- < \text{NCS}^- < \text{C}_6\text{H}_5^-$       (b)  $\text{C}_6\text{H}_5^- < \text{Cl}^- < \text{C}_2\text{H}_5\text{OH} < \text{NCS}^-$   
(c)  $\text{C}_2\text{H}_5\text{OH} < \text{Cl}^- < \text{NCS}^- < \text{C}_6\text{H}_5^-$       (d)  $\text{Cl}^- < \text{C}_2\text{H}_5\text{OH} < \text{NCS}^- < \text{C}_6\text{H}_5^-$
- The CFSE for the following  $d^3$  metal ions ( $\text{V}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mo}^{3+}$ ) decreases in the following order :-  
(a)  $\text{V}^{2+} > \text{Cr}^{3+} > \text{Mo}^{3+}$       (b)  $\text{Cr}^{3+} > \text{V}^{2+} > \text{Mo}^{3+}$       (c)  $\text{Mo}^{3+} > \text{Cr}^{3+} > \text{V}^{2+}$       (d)  $\text{Cr}^{3+} > \text{Mo}^{3+} > \text{V}^{2+}$
- Which order of CFSE is correct for the geometry of complex :-  
(a)  $\Delta_{\text{ICS}} < \Delta_t < \Delta_c < \Delta_o < \Delta_{\text{sp}}$       (b)  $\Delta_{\text{sp}} < \Delta_o < \Delta_c < \Delta_t < \Delta_{\text{ICS}}$
- The CFSE for the following metal ions increases in the following order :  
(a)  $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Co}^{3+} < \text{Rh}^{3+}$       (b)  $\text{Rh}^{3+} < \text{Co}^{3+} < \text{Cr}^{3+} < \text{Mn}^{2+}$   
(c)  $\text{Cr}^{3+} < \text{Mn}^{2+} < \text{Co}^{3+} < \text{Rh}^{3+}$       (d)  $\text{Co}^{3+} < \text{Rh}^{3+} < \text{Mn}^{2+} < \text{Cr}^{3+}$

10. For which d-electron set more than one spin value can be possible.  
 (a)  $d^1/d^2/d^3$  (b)  $d^4/d^5/d^6/d^7$  (c)  $d^8/d^9/d^{10}$  (d) all of these
11. In the complex  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , water act as:  
 (a) strong field ligand (b) weak field ligand (c) both (d) none of these
12. Strong field ligands such as  $\text{CN}^-$ :-  
 (a) Usually produce high spin complexes and small crystal field splittings.  
 (b) Usually produce low spin complexes and high crystal field splittings.  
 (c) Usually produce high spin and high crystal field splittings.  
 (d) Usually produce low high and small crystal field splittings.
13. Crystal field stabilization energy for high spin  $d^4$  octahedral complex is  
 (a)  $-1.8 \Delta_0$   
 (b)  $-1.6 \Delta_0$   
 (c)  $-1.2 \Delta_0$   
 (d)  $-0.6 \Delta_0$
14. What is correct order of crystal field splitting in complexes.  
 $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Rh}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ir}(\text{NH}_3)_6]^{3+}$   
 (a)  $[\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Rh}(\text{NH}_3)_6]^{3+} > [\text{Ir}(\text{NH}_3)_6]^{3+}$   
 (b)  $[\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Rh}(\text{NH}_3)_6]^{3+} < [\text{Ir}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Rh}(\text{NH}_3)_6]^{3+} = [\text{Ir}(\text{NH}_3)_6]^{3+}$   
 (d)  $[\text{Co}(\text{NH}_3)_6]^{3+} = [\text{Rh}(\text{NH}_3)_6]^{3+} = [\text{Ir}(\text{NH}_3)_6]^{3+}$
15. What is correct order of crystal field splitting in the following complexes.  
 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{ox})_3]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$   
 (a)  $[\text{Fe}(\text{CN})_6]^{3-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{Fe}(\text{ox})_3]^{3-} > [\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   
 (b)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{Fe}(\text{CN})_6]^{3-} > [\text{Fe}(\text{ox})_3]^{3-} > [\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{3-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{Fe}(\text{H}_2\text{O})_6]^{3+} > [\text{Fe}(\text{ox})_3]^{3-}$   
 (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} > [\text{Fe}(\text{ox})_3]^{3-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{Fe}(\text{CN})_6]^{3-}$
16. Which of the following statements is correct on the basis of given data?

Complex	$\Delta_0$	P
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$\Delta_1$	$P_1$
$[\text{Co}(\text{NH}_3)_6]^{2+}$	$\Delta_2$	$P_2$
$[\text{Rh}(\text{H}_2\text{O})_6]^{2+}$	$\Delta_3$	$P_3$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$\Delta_4$	$P_4$



- (a)  $\Delta_1 = \Delta_2 = \Delta_3 = \Delta_4$  (b)  $\Delta_1 \neq \Delta_2 \neq \Delta_3 \neq \Delta_4$   
 (c)  $P_1 = P_2 \neq P_3 \neq P_4$  (d)  $P_1 = P_2 = P_4 \neq P_3$
17. Which of the following option is correct?  
 (a)  $\Delta_t = \frac{4}{9} \Delta_o$  (b)  $\Delta_c = \frac{8}{9} \Delta_o$   
 (c)  $\Delta_{sp} \approx (1.2 \Delta_o - 2\Delta_o)$  (d)  $\Delta_{icosahedral} = 0$
18. On which factor the magnitude of  $\Delta$  depends:  
 (a) Oxidation state of metal cation (b) Different d-electrons  
 (c) Principle quantum no. of d-orbital (d) nature of ligand
19. From the following pair of complex in how many set of complexes the first complex would have greater value of  $\Delta_o$   
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{CrF}_6]^{3-}$  and  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{en})_3]^{2+}$   
 (e)  $[\text{ReF}_6]^{2-}$  and  $[\text{MnF}_6]^{2-}$  (f)  $[\text{Rh}(\text{en})_3]^{3+}$  and  $[\text{Co}(\text{en})_3]^{3+}$
20. How many unpaired electrons are there in a strong field iron (II) octahedral complex?

### ANSWER KEY

- |         |           |               |               |             |         |         |
|---------|-----------|---------------|---------------|-------------|---------|---------|
| 1. (a)  | 2. (d)    | 3. (b)        | 4. (b)        | 5. (b)      | 6. (d)  | 7. (c)  |
| 8. (a)  | 9. (a)    | 10. (b)       | 11. (d)       | 12. (b)     | 13. (d) | 14. (b) |
| 15. (a) | 16. (b,c) | 17. (a,b,c,d) | 18. (a,b,c,d) | 19. (c,e,f) | 20. (0) |         |

## HINTS & SOLUTION

**1Sol.** 5d series metal complex have greater splitting energy as compared to 3d series metal. From  $[\text{Co}(\text{CN})_6]^{3-}$  and  $[\text{CoCl}_6]^{3-}$  CN is strong field ligand. So splitting will be more in case of  $[\text{Co}(\text{CN})_6]^{3-}$ .

Correct order is (i) < (ii) < (iii) correct option is (a)

**2Sol.** Spectrochemical series is

$\text{I}^- < \text{Br}^- < \text{S}_2^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$ ,  $\text{F}^- < \text{urea}$ ,  $\text{OH}^- < \text{Ox}$ ,  $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$ ,  $\text{NH}_3 < \text{en} < \text{bpy}$ ,  $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$ ,  $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$

So, correct option is (d)

**3Sol.** Order of splitting energy is

$\text{Rh}^{3+} > \text{Co}^{3+} > \text{Co}^{2+}$

Correct option is (b)

**4Sol.** Here oxidation state of Iron is +3 and X behave as strong field ligand as it has one unpaired electron.

Option (b) is correct.

**5Sol.**  $[\text{Co}(\text{NH}_3)_6]^{3+} \rightarrow \text{Co}^{3+} \rightarrow d^6$

$[\text{Ir}(\text{NH}_3)_6]^{3+} \rightarrow \text{Ir}^{3+} \rightarrow d^6$

$[\text{Fe}(\text{bpy})_3]^{3+} \rightarrow \text{Fe}^{3+} \rightarrow d^5$

$[\text{Fe}(\text{NH}_3)_6]^{2+} \rightarrow \text{Fe}^{2+} \rightarrow d^6$

\* highest the oxidation state of metal ion higher will be  $\Delta_o$ .

\* metal cation with the same oxidation states but different no. of d-electrons, the magnitude of  $\Delta_o$  decrease with increase in the no. of d-electrons.

\* on going  $3d \rightarrow 4d \rightarrow 5d$ ,  $\Delta$  will be increase.

\*  $\text{NH}_3 < \text{bpy}$

Option (b) is correct.

**6Sol.** Option (d) is correct increasing order of CFSE is  $\text{Cl}^- < \text{C}_2\text{H}_5\text{OH} < \text{NCS}^- < \text{C}_6\text{H}_5^-$ .

**7Sol.** Option (c) is correct because when oxidation state increases crystal field stabilization energy increases & when  $3d \rightarrow 4d \rightarrow 5d$  going CFSF will increases.

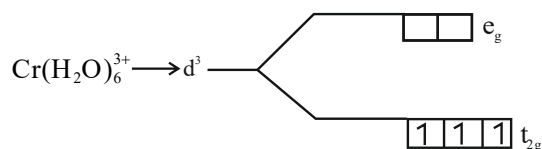
$\text{V}^{2+} < \text{Cr}^{3+} < \text{Mo}^{3+}$

**8Sol.** Option (a) is correct because the correct order of CFSE is  $\Delta_{\text{ICS}} < \Delta_t < \Delta_c < \Delta_o < \Delta_{\text{sp}}$ .

**9Sol.** Option (a) is correct because when oxidation state increase CFSE increases & when  $d^e$  increases CFSE decreases.

**10Sol.** Option (b) is correct high spin or low spin phenomenon found in only  $d^4/d^5/d^6/d^7$  electrons.

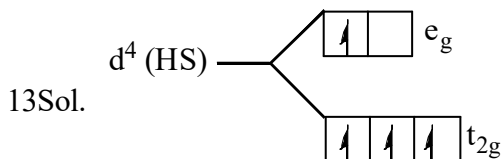
**11Sol.** Option (d) none of these.



in  $d^1/d^2/d^3/d^8/d^9/d^{10}$  there is no role of strong & weak field ligand phenomenon.

**12Sol.**  $\text{CN}^-$  is strong field so it usually produce low spin complexes and high crystal field splittings.

Correct option is (b).



$$\begin{aligned} \text{CFSE} &= -0.4 \times 3 + 0.6 \times 1 \\ &= -1.2 + 0.6 \end{aligned}$$

**14.Sol.** As we move from the series  $3d \rightarrow 4d \rightarrow 5d$  crystal field splitting increases.

So, correct order is

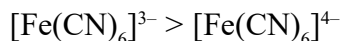


Correct option is (b)

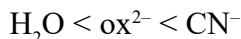
$$= -0.6 \Delta_0$$

Correct option is (d)

**15.Sol.** As the oxidation state of metal ion increases crystal field splitting increases. Therefore



crystal field splitting also depends upon field of ligand and varies according to spectrochemical series.



Therefore correct order is (a)

**16.Sol.**  $\Delta_0$  depends upon ligand and metal ion So,  $\Delta_0$  will be different for each metal complex.

Pairing energy depends only on metal ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Co}(\text{NH}_3)_6]^{2+}$  both will have same pairing energy.

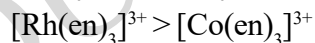
So, (b) and (c) are correct.

**17.Sol.** a, b, c, d

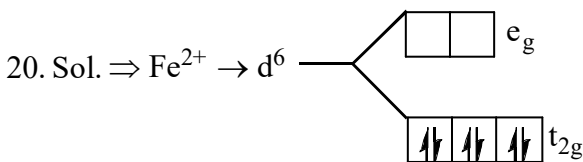
All the statement are correct.

**18.Sol.** All of these option are correct because magnitude of  $\Delta$  depends on oxidation state, nature of ligand, principle quantum no. of d-orbital & different d-electrons.

**19. Sol.**  $[\text{Fe}(\text{CN})_6]^{3-} > [\text{Fe}(\text{CN})_6]^{4-}$



So, correct answer is (3)



There is no unpaired electron in  $\text{Fe}(\text{II})$ .

Correct answer is 0



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (9)

- CFSE of transition metal complexes can be determined by:  
(a) UV-Visible spectroscopy (b) IR spectroscopy  
(c) Microwave spectroscopy (d) NMR spectroscopy
- CFSE is calculated with reference to:  
(a)  $d_{(GS)}$  (b)  $d_{(ES)}$  (c)  $t_{2g}$  (d)  $e_g$
- Total stabilization energy is:  
(a) Only CFSE (b) Only JTSE  
(c) Sum of CFSE and JTSE both (d) None of these
- For a complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  what will be the value of CFSE  
(a)  $-0.8\Delta_o + P$  (b)  $-1.2\Delta_o + P$  (c)  $-0.4\Delta_o + P$  (d)  $+0.4\Delta_o + P$
- The crystal field stabilization energy (CFSE), in unit of  $\Delta_o$  for  $[\text{CoF}_3(\text{H}_2\text{O})_3]$  is:  
(a) 0 (b) 0.4 (c) 0.8 (d) 1.8
- For  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  shows absorption maximum at 580 nm what is the CFSE in kJ/mol.  
(a) 72.36 kJ/mol (b) -82.396 kJ/mol (c) -72.36 kJ/mol (d) 82.396 kJ/mol
- Correct increasing order of the wavelength of absorption in the visible region for the complexes of  $\text{Co}^{3+}$  is  
(a)  $[\text{Co}(\text{CN})_6]^{3-} > [\text{Co}(\text{en})_3]^{3+} > [\text{Co}(\text{NH}_3)_6]^{3+}$   
(b)  $[\text{Co}(\text{en})_3]^{3+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{CN})_6]^{3-}$   
(c)  $[\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{en})_3]^{3+} > [\text{Co}(\text{CN})_6]^{3-}$   
(d)  $[\text{Co}(\text{CN})_6]^{3-} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{en})_3]^{3+}$
- Among the following complexes the one which show zero crystal field stabilisation energy (CFSE) is:  
(a)  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- In which of the following coordination entities the magnitude of  $\Delta_{\text{oh}}$  CFSE in octahedral field will be maximum?  
(Atomic number Co = 27)  
(a)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (c)  $[\text{Co}(\text{CN})_6]^{3-}$  (d)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

10. Among the following pairs of complexes, in which case the  $\Delta_o$  value is higher for the first one?  
 (a)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{CN})_6]^{3-}$  (b)  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
11. What is an electronic arrangement of metal atom/ionic octahedral complex with  $d^4$  configuration, if  $\Delta_o >$  pairing energy?  
 (a)  $t_{2g}^4 e_g^0$  (b)  $e_g^4 t_{2g}^0$  (c)  $t_{2g}^3 e_g^1$  (d)  $e_g^2 t_{2g}^2$
12. What is the correct electronic configuration of the central atom in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  based on crystal field theory?  
 (a)  $e_g^4 t_{2g}^2$  (b)  $t_{2g}^4 e_g^2$  (c)  $t_{2g}^6 e_g^0$  (d)  $e_g^3 t_{2g}^3$
13. The crystal field stabilization energies (CFSE) of high spin and low spin  $d^6$  metal complexes in terms of  $\Delta_o$  respectively are  
 (a)  $-0.4$  and  $-2.4$  (b)  $-2.4$  and  $-0.4$  (c)  $-0.4$  and  $0.0$  (d)  $-2.4$  and  $0.0$
14. Complexes of first row transition metal having tetrahedral geometry are high spin due to-  
 (a)  $\Delta_t > P$  (b)  $\Delta_t < P$  (c)  $\Delta_t = P$  (d)  $\Delta_t > \Delta_o$
15. The crystal field stabilization energy of high spin  $d^7$  octahedral complex.  
 (a)  $-0.8 \Delta_o$  (b)  $-0.8 \Delta_o + 3P$  (c)  $-1.8 \Delta_o + 2P$  (d)  $-1.8 \Delta_o + 3P$
16. The complex with maximum CFSE is:  
 (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (c)  $[\text{Fe}(\text{CN})_6]^{4-}$  (d)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
17.  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  differ in:  
 (a) Magnetic moment (b) CFSE value  
 (c) Hybridization (d) Oxidation state
18. For which of the following  $d^n$  configuration of octahedral complexes, can not exist in both high spin and low spin forms:  
 (a)  $d^3$  (b)  $d^5$  (c)  $d^6$  (d)  $d^8$
19. The crystal field splitting energy ( $\Delta$ ) for  $[\text{Co}(\text{NH}_3)_6]^{2+}$  is 10,200. The  $\Delta$  for  $[\text{Co}(\text{NH}_3)_4]^{2+}$ .
20.  $\Delta_o$  value for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is  $14,000 \text{ cm}^{-1}$ . Calculate crystal field splitting energy for the complex.

## ANSWER KEY

- |            |            |                  |                  |            |         |         |
|------------|------------|------------------|------------------|------------|---------|---------|
| 1. (a)     | 2. (b)     | 3. (c)           | 4. (c)           | 5. (b)     | 6. (b)  | 7. (c)  |
| 8. (b)     | 9. (c)     | 10. (d)          | 11. (a)          | 12. (c)    | 13. (a) | 14. (b) |
| 15. (a)    | 16. (a, c) | 17. (a, b, c, d) | 18. (a, b, c, d) | 19. 4533.3 |         |         |
| 20. 14,000 |            |                  |                  |            |         |         |

## HINTS & SOLUTION

**1.Sol.** CFSE of transition metal complexes can be determined by UV-visible spectroscopy.

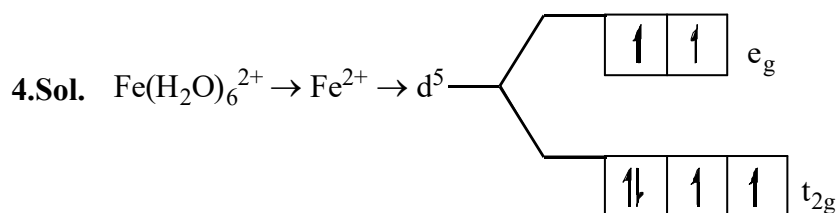
Correct option is (a)

**2.Sol.** CFSE is calculated with reference of excited state of d-orbital.

Correct option is (b)

**3.Sol.** Total stabilization energy is crystal field splitting and Jahn teller splitting energy both.

Correct option is (c)



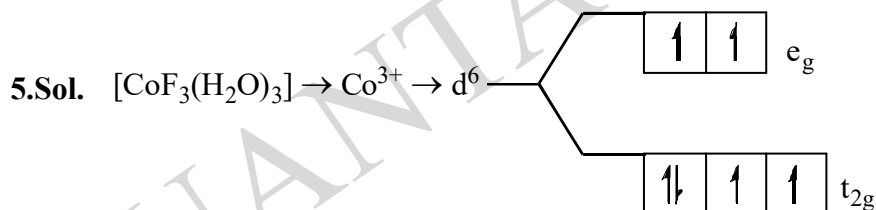
$$(-0.4 \times 4 + 0.6 \times 2) \Delta_o$$

$$(-1.6 + 1.2) \Delta_o$$

$$(-0.4) \Delta_o$$

In this all the answer is with pairing energy. So it is consider in the solution.

Correct option is (c)

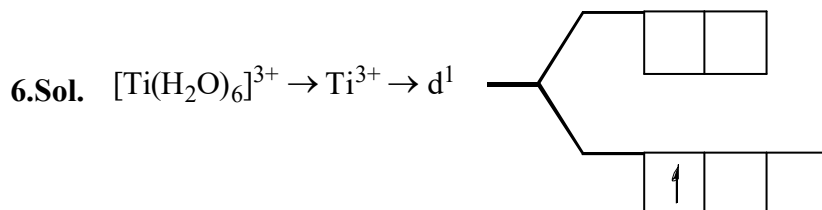


$$\text{CFSE} = (-0.4 \times 4 + 0.6 \times 2) \Delta_o$$

$$= (-1.6 + 1.2) \Delta_o = -0.4 \Delta_o$$

$$\text{CFSE} = 0.4 \Delta_o$$

Correct option is (b)



$$\text{CFSE} = -0.4 \Delta_o$$

$$\lambda = 580 \text{ nm}$$

$$(\Delta_o) \text{ cm}^{-1} = \frac{1}{\lambda} = \frac{10^7}{580 \text{ cm}}$$

$$= \frac{1000 \times 10^4}{580} = 1.724 \times 10^4 \text{ cm}^{-1}$$

$$\text{CFSE} = -0.4 \times 1.724 \times 10^4 \text{ cm}^{-1}$$

$$= \left( \frac{-0.4 \times 1.724 \times 10^4}{83.7} \right) \text{ kJ/mol}$$

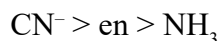
$$= \left( \frac{-0.6896 \times 10^4}{83.7} \right)$$

$$= -82.396 \text{ kJ/mol.}$$

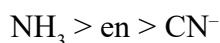
Correct option is (b)

**7.Sol.** Wavelength  $\propto \frac{1}{\text{Energy}}$

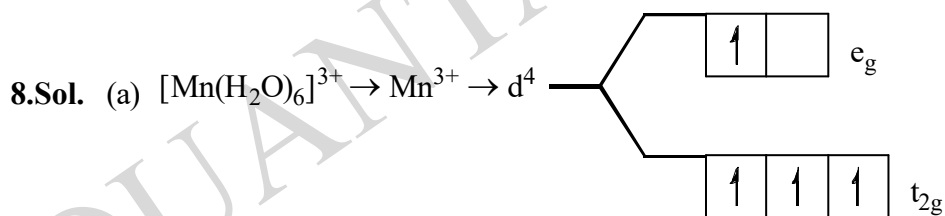
So according to spectrochemical series crystal field splitting order is



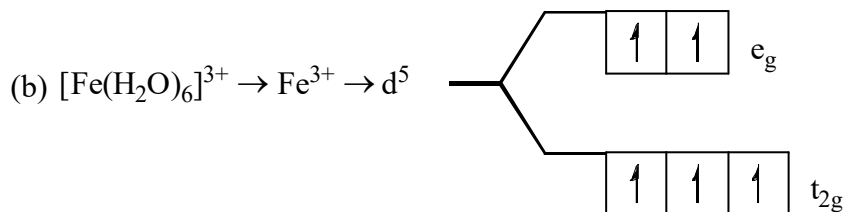
and wavelength order will be



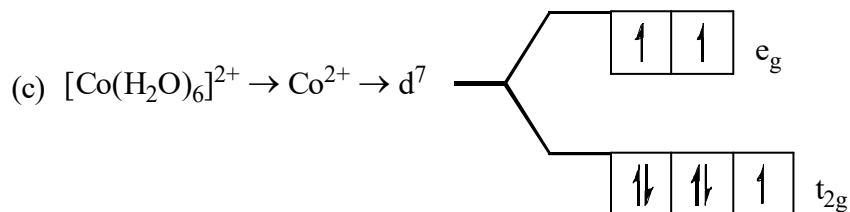
Correct option is (c)



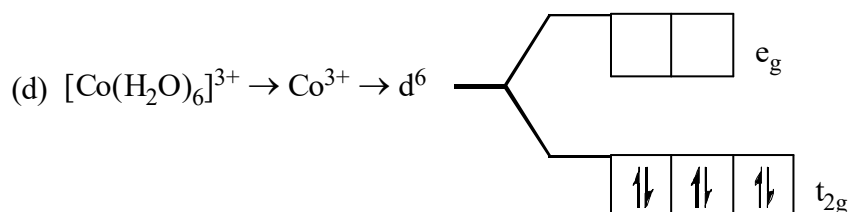
$$\begin{aligned} \text{CFSE} &= [3 \times (-0.4) + 0.6 \times 1] \Delta_o \\ &= (-1.2 + 0.6) \Delta_o \\ &= -0.6 \Delta_o \end{aligned}$$



$$\begin{aligned} \text{CFSE} &= [3 \times (-0.4) + 2 \times 0.6] \Delta_o \\ &= (-1.2 + 1.2) \Delta_o = 0 \Delta_o \end{aligned}$$



$$\begin{aligned}\text{CFSE} &= [5 \times (-0.4) + 0.6 \times 2] \Delta_o \\ &= (-2.0 + 1.2) \Delta_o = -0.8 \Delta_o\end{aligned}$$



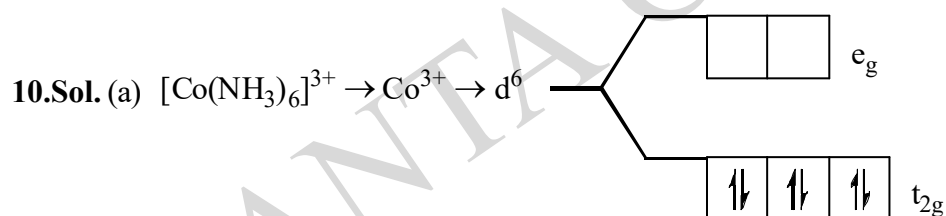
$$\begin{aligned}\text{CFSE} &= [6 \times (-0.4) + 0.6 \times 0] \Delta_o \\ &= -2.4 \Delta_o\end{aligned}$$

Correct option is (b)

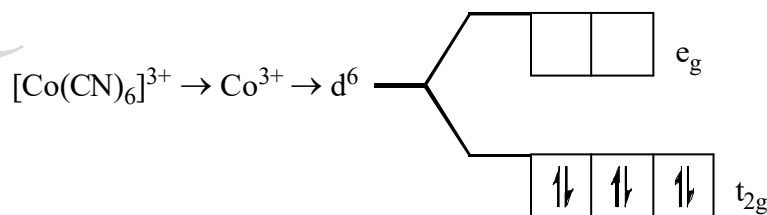
**9.Sol.** According to spectrochemical series crystal field splitting energy order is  $\text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{CN}^-$

So the magnitude of  $\Delta_{\text{oh}}$  is maximum in  $[\text{Co}(\text{CN})_6]^{3-}$

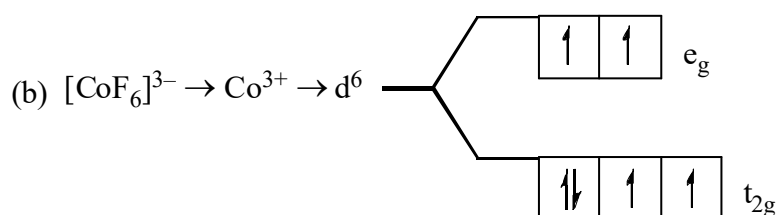
Correct option is (c)



$$\begin{aligned}\text{CFSE} &= (-0.4 \times 6 + 0.6 \times 0) \Delta_o \\ &= (-2.4 + 0) \Delta_o = -2.4 \Delta_o\end{aligned}$$

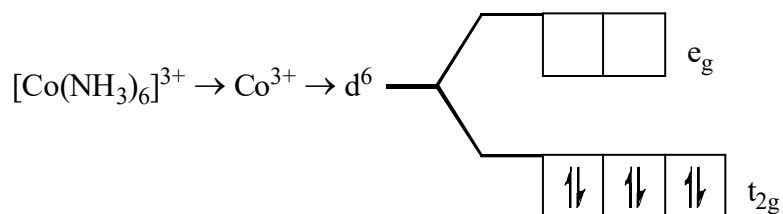


$$\begin{aligned}\text{CFSE} &= (-0.4 \times 6 + 0.6 \times 0) \Delta_o \\ &= -2.4 \Delta_o\end{aligned}$$

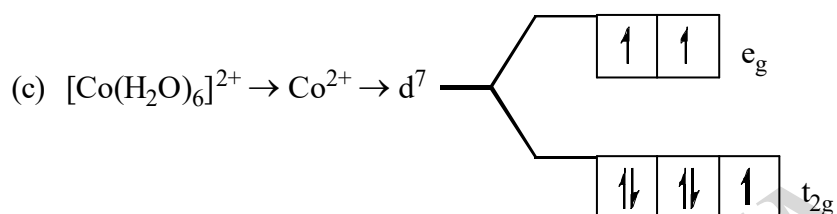




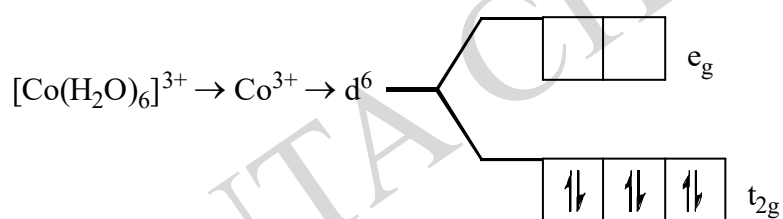
$$\begin{aligned}\text{CFSE} &= (-0.4 \times 4 + 0.6 \times 2)\Delta_o \\ &= (-1.6 + 1.2)\Delta_o = -0.4 \Delta_o\end{aligned}$$



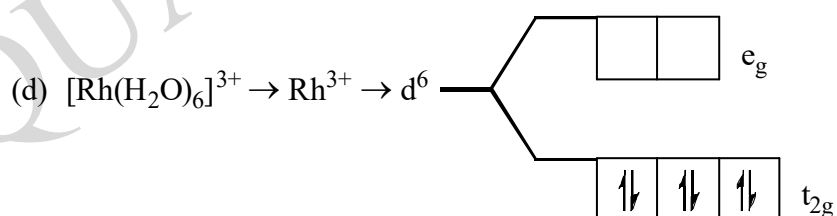
$$\begin{aligned}\text{CFSE} &= (-0.4 \times 6 + 0.6 \times 0)\Delta_o \\ &= -2.4 \Delta_o\end{aligned}$$



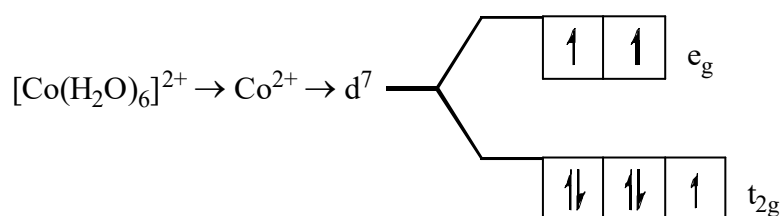
$$\begin{aligned}\text{CFSE} &= (-0.4 \times 5 + 0.6 \times 2)\Delta_o \\ &= (-2.0 + 1.2)\Delta_o = -0.8 \Delta_o\end{aligned}$$



$$\begin{aligned}\text{CFSE} &= (-0.4 \times 6 + 0.6 \times 0)\Delta_o \\ &= -2.4 \Delta_o\end{aligned}$$



$$\begin{aligned}\text{CFSE} &= (-0.4 \times 6 + 0.6 \times 0)\Delta_o \\ &= -2.4 \Delta_o\end{aligned}$$

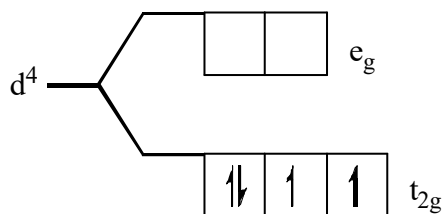


$$\begin{aligned}\text{CFSE} &= (-0.4 \times 5 + 0.6 \times 2)\Delta_o \\ &= (-2.0 + 1.2)\Delta_o = -0.8 \Delta_o\end{aligned}$$

Option (d) is correct because in this case CFSE value is highest for the first one.

Correct option is (d)

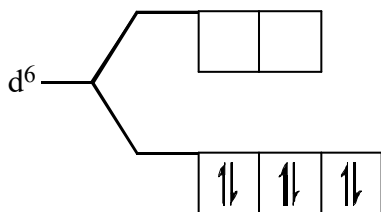
11.Sol. If  $\Delta_o$  is greater than pairing energy then electron get paired and form low spin complex.



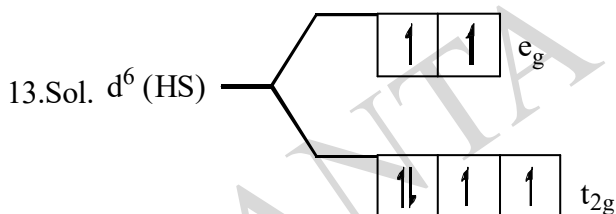
$$\begin{aligned}\text{CFSE} &= [-0.4 \times 4 + 0.6 \times 0]\Delta_o + P \\ &= -1.6 \Delta_o + P\end{aligned}$$

12.Sol.  $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

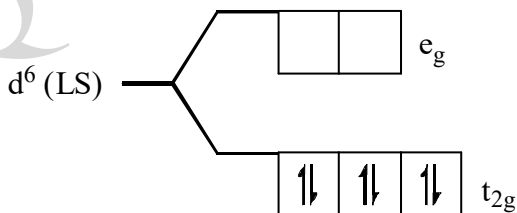
$[Fe(CN)_6]^{4-} \rightarrow Fe^{2+} \rightarrow d^6 \rightarrow CN^- \rightarrow \text{low spin}$



Correct option is (c)



$$\begin{aligned}\text{CFSE} &= (-0.4 \times 4 + 0.6 \times 2)\Delta_o \\ &= (-1.6 + 1.2)\Delta_o = -0.4 \Delta_o\end{aligned}$$



$$\begin{aligned}\text{CFSE} &= (-0.4 \times 6 + 0.6 \times 0)\Delta_o \\ &= -2.4 \Delta_o\end{aligned}$$

Correct option is (a)

14.Sol.  $\Delta_t < P$

Because if pairing energy is high  $e^-$  remain unpaired and thus form high spin complex.

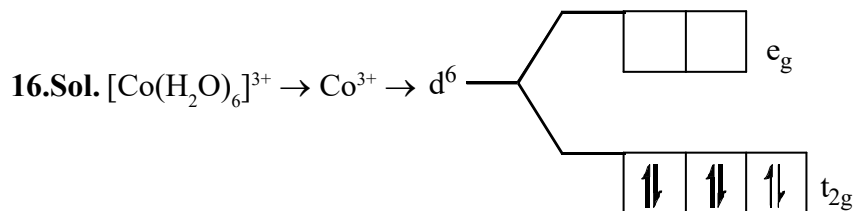
Correct option is (b)

15.Sol. High spin  $d^7 - t_{2g}^5 e_g^2$

$$CFSE = [- (5 \times 0.4) + (2 \times 0.6)] \Delta_0$$

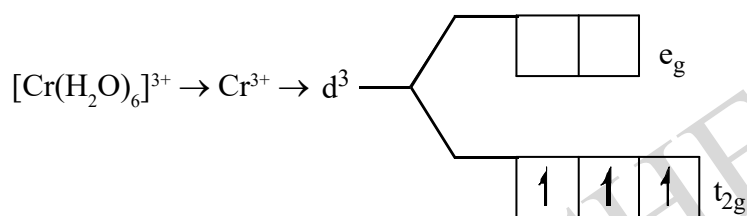
$$= \boxed{-0.8\Delta_0}$$

Correct option is (a)



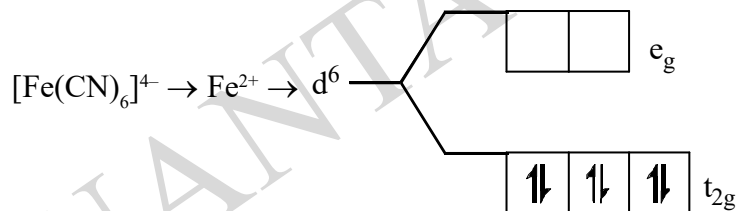
$$CFSE = -0.4 \times 6 + 0 \times 0.6$$

$$= -2.4 \Delta_0$$



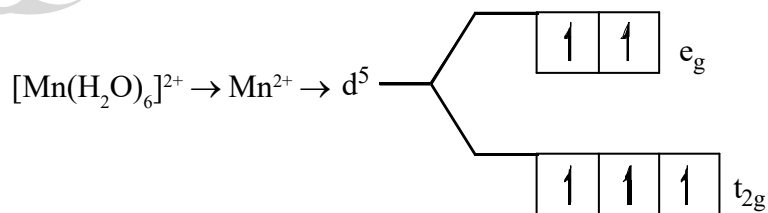
$$CFSE = -0.4 \times 3 + 0.6 \times 0$$

$$= -1.2 \Delta_0$$



$$CFSE = -0.4 \times 6 + 0.6 \times 0$$

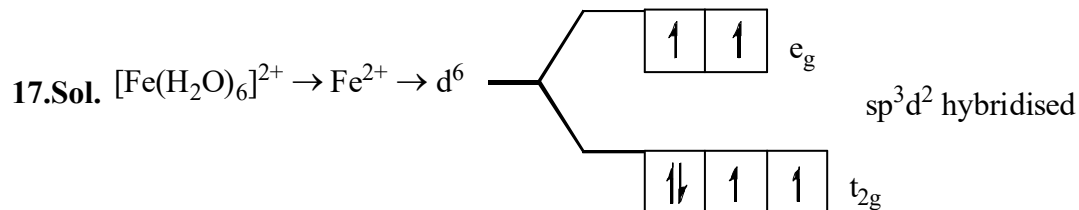
$$= -2.4 \Delta_0$$



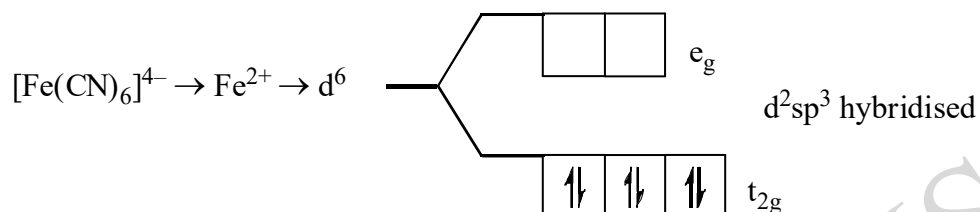
$$CFSE = -0.4 \times 3 + 0.6 \times 2$$

$$= -1.2 + 1.2 = 0$$

Correct option is (a, c)



$$\begin{aligned}\text{CFSE} &= (-0.4 \times 4 + 0.6 \times 2)\Delta_o \\ &= -1.6 + 1.2 = -0.4 \Delta_o\end{aligned}$$



$$\begin{aligned}\text{CFSE} &= (-0.4 \times 6 + 0.6 \times 0)\Delta_o \\ &= -2.4 \Delta_o\end{aligned}$$

Correct options are (a, b, c, d)

**18.Sol.** Option (a, d) is correct because high spin/low spin forms does not used for  $d^1/d^2/d^3/d^8/d^9/d^{10}$ . High spin/low spin form used only for  $d^4/d^5/d^6/d^7$ .

Correct option is (c)

**19.Sol.**  $\Delta_t = \frac{4}{9}\Delta_o$

$$= \frac{4}{9} \times 10,200 = 4533.3 \text{ cm}^{-1}$$

**20.Sol.** Crystal field splitting energy is  $\Delta_o$ . So  $\Delta_o$  value will be same for crystal field splitting energy.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (11)

- Which of the following value of  $\lambda$  is not possible for any spinel.  
(a) zero (b) 0.45 (c) 1 (d) 0.5
- Which of the following metal ion generally from inverse spinel.  
(a)  $\text{Cr}^{3+}$  (b)  $\text{Co}^{3+}$  (c)  $\text{Fe}^{3+}$  (d)  $\text{Al}^{3+}$
- Which of the following is inverse spinel.  
(a)  $\text{ZnFe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4$  (c)  $\text{FeCr}_2\text{O}_4$  (d)  $\text{Mn}_3\text{O}_4$
- Which of the following is normal spinel.  
(a)  $\text{ZnFe}_2\text{O}_4$  (b)  $\text{NiGa}_2\text{O}_4$  (c)  $\text{CoFe}_2\text{O}_4$  (d)  $\text{FeFe}_2\text{O}_4$
- What is the value of  $\lambda$  for  $\text{ZnFe}_2\text{O}_4$   
(a) Zero (b) 0.5 (c) 0.9 (d) 1
- Calculate occupancy of  $\text{Fe}^{3+}$  ion in  $T_d$  void in a spinel  $\text{MnFe}_2\text{O}_4$  having  $\lambda = 0.15$
- For the spinel  $\text{ZnFe}_2\text{O}_4$  what is hybridisation of  $\text{Fe}^{3+}$  ion  
(a)  $\text{sp}^3$  (b)  $\text{sp}^3\text{d}^2$  (c)  $\text{d}^2\text{sp}^3$  (d)  $\text{sp}^3$  and  $\text{sp}^3\text{d}^2$  both
- The spinels  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  respectively are  
(a) Both inverse (b) Both normal (c) Inverse normal (d) Normal and inverse
- For the spinel  $\text{MnFe}_2\text{O}_4$  what is hybridisation of  $\text{Fe}^{3+}$  ion.  
(a)  $\text{sp}^3$  (b)  $\text{sp}^3$  (c)  $\text{d}^2\text{sp}^3$  (d)  $\text{sp}^3$  and  $\text{sp}^3\text{d}^2$  both
- $\text{Fe}^{3+}$  ions from normal spinel with which of the following ions.  
(a)  $\text{Mg}^{2+}$  (b)  $\text{Mn}^{2+}$  (c)  $\text{Zn}^{2+}$  (d)  $\text{Cu}^{2+}$
- What is the correct order of inverse character in spinel.  
(a)  $\text{Mn}_3\text{O}_4 < \text{MgFe}_2\text{O}_4 < \text{MnFe}_2\text{O}_4 < \text{NiAl}_2\text{O}_4 < \text{Mn}_3\text{O}_4$   
(b)  $\text{Mn}_3\text{O}_4 < \text{MnFe}_2\text{O}_4 < \text{NiAl}_2\text{O}_4 < \text{MgFe}_2\text{O}_4 < \text{Mn}_3\text{O}_4$   
(c)  $\text{Mn}_3\text{O}_4 < \text{NiAl}_2\text{O}_4 = \text{NiAl}_2\text{O}_4 = \text{MgFe}_2\text{O}_4 < \text{Mn}_3\text{O}_4$   
(d)  $\text{Mn}_3\text{O}_4 < \text{NiAl}_2\text{O}_4 < \text{MnFe}_2\text{O}_4 < \text{MgFe}_2\text{O}_4 < \text{Mn}_3\text{O}_4$

12. Which of the following shows normal spinel structure?  
 (a)  $\text{Fe}_3\text{O}_4$  (b)  $\text{Mn}_3\text{O}_4$  (c)  $\text{NiAl}_2\text{O}_4$  (d)  $\text{CuLa}_2\text{O}_4$
13. Among the compounds  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  and  $\text{Mn}_3\text{O}_4$   
 (a)  $\text{NiFe}_2\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  are normal spinels (b)  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  are normal spinels  
 (c)  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  are inverse spinels (d)  $\text{Fe}_3\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  are inverse spinels
14.  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$  are metal oxides having spinel structure. Considering their CFSE, the correct statement regarding their structure is  
 (a) both have normal spinel structure (b) both have inverse spinel structure  
 (c)  $\text{Fe}_3\text{O}_4$  has a normal and  $\text{Co}_3\text{O}_4$  are inverse spinels  
 (d)  $\text{Fe}_3\text{O}_4$  has a inverse and  $\text{Co}_3\text{O}_4$  are normal spinels
15. Which of the following metal ions generally form normal spinel.  
 (a)  $\text{Cr}^{3+}$  (b)  $\text{Co}^{3+}$  (c)  $\text{Fe}^{3+}$  (d)  $\text{Al}^{3+}$
16. Which of the following statements are true for spinel.  
 (a) In case of normal spinel bivalent ions occupy tetrahedral sites and trivalent ions occupy octahedral sites.  
 (b) In case of inverse spinel all bivalent cations are present in tetrahedral voids  
 (c) Since oxides ions are weak field ligands, the cation are found in high spin configurations.  
 (d) All of these
17. What is oxidation number of Fe in  $\text{Fe}_3\text{O}_4$   
 (a) +2 (b) +3 (c)  $8/3$  (d) zero
18.  $\text{Al}^{3+}$  ions from normal spinel with which of the following ions.  
 (a)  $\text{Mg}^{2+}$  (b)  $\text{Ni}^{2+}$  (c)  $\text{Co}^{2+}$  (d) All of these
19. For a given spinel  $\text{AB}_2\text{O}_4$ ,  $\lambda = 0.17$ . Calculate in what percent inversion take place.
20. How many from the following are partially inverse spinels.  
 $\text{MnFe}_2\text{O}_4$ ,  $\text{NiAl}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$
21. How many spinel from the following are normal?  
 $\text{MnAl}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$

## ANSWER KEY

- |               |            |            |            |         |         |         |
|---------------|------------|------------|------------|---------|---------|---------|
| 1. (c)        | 2. (c)     | 3. (b)     | 4. (a)     | 5. (a)  | 6. (0)  | 7. (b)  |
| 8. (a)        | 9. (d)     | 10. (c)    | 11. (b)    | 12. (b) | 13. (d) | 14. (d) |
| 15. (a, b, d) | 16. (a, c) | 17. (a, b) | 18. (d, c) | 19. 34% | 20. 3   |         |
| 21. 4         |            |            |            |         |         |         |

## HINTS & SOLUTION

- 1.Sol. As the value of  $\lambda$  lies between 0 to 0.5. So  $\lambda = 1$  not possible for any spinel.
- 2.Sol.  $\text{Fe}^{3+}$  ion has  $d^5$  configuration and form high spin complex. Therefore it will have zero CFSE. So, it will form inverse spinel.
- 3.Sol.  $\text{CoFe}_2\text{O}_4$  will form inverse spinel as  $\text{Co}^{2+}$  has large CFSE value.
- 4.Sol. As in  $\text{ZnFe}_2\text{O}_4$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$  both have zero CFSE and form normal spinel.
- 5.Sol.  $\text{ZnFe}_2\text{O}_4$  will form normal spinel so  $\lambda = 0$ .
- 6.Sol.  $\% \text{ inverse} = \frac{\lambda}{0.5} \times 100 = \frac{0.15}{0.5} \times 100 = 30\%$   
 $\begin{matrix} & & & \text{T}_d & & \text{O}_h \\ \text{In case of normal spinel} & \text{Mn}^{2+} & 2\text{Fe}^{3+} & & & \end{matrix}$   
 $\begin{matrix} \text{Fe}^{3+} = 0.3 & \text{Mn}^{2+} = 0.3 \\ \text{Mn}^{2+} = 0.7 & \text{Fe}^{3+} = 1.7 \end{matrix}$   
 When 30% inversion take place  
 $\text{Fe}^{3+} \text{ in tetrahedral void} = \frac{0.3}{8} \times 100 = 3.75\%$
- 7.Sol. As the given spinel  $\text{ZnFe}_2\text{O}_4$  is normal. So,  $\text{Zn}^{2+}$  will lie in tetrahedral void and  $\text{Fe}^{3+}$  ions will lie in octahedral voids. So, hybridisation will be  $sp^3d^2$ .
- 8.Sol. As  $\text{Fe}^{3+}$  ion in both spinel have zero CFSE so, other ions  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  have more tendency to occupy octahedral site and will form inverse spinel.
- 9.Sol. As the given spinel is partial inverse spinel. So,  $\text{Fe}^{3+}$  will in octahedral as well as tetrahedral voids. In octahedral void its hybridisation will be  $sp^3d^2$  and in tetrahedral void hybridisation will be  $sp^3$ .
- 10.Sol.  $\text{Zn}^{2+}$  ion have zero CFSE so, it form normal spinel with  $\text{Fe}^{3+}$  ion.
- 11.Sol. 

$\text{Fe}_3\text{O}_4$	$\text{Mn}_3\text{O}_4$	$\text{MnFe}_2\text{O}_4$	$\text{NiAl}_2\text{O}_4$	$\text{MgFe}_2\text{O}_4$
$\lambda = 0.5$	$\lambda = 0$	$\lambda = 0.1$	$\lambda = 0.38$	$\lambda = 0.45$

As in case of  $\text{MnFe}_2\text{O}_4$  both are transition element inverse character will be less. In case of  $\text{NiAl}_2\text{O}_4$  transition element Nickel is replacing  $\text{Al}^{3+}$ , a non transition element so inversion will not take place to much extend. But in case of  $\text{MgFe}_2\text{O}_4$   $\text{Mg}^{2+}$  which has high lattice energy can easily replace transition element. Therefore inversion will be more

So, correct option is (b)

- 12.Sol.  $\text{Mn}_3\text{O}_4$  will form normal spinel

- 13.Sol.  $\text{FeFe}_2\text{O}_4$  is inverse type spinel, because CFSE of  $\text{Fe}^{2+}$  is more than  $\text{Fe}^{3+}$  in octahedral site.

$\text{NiFe}_2\text{O}_4$  is also inverse type spinel. because CFSE of  $\text{Ni}^{2+}$  is more than  $\text{Fe}^{3+}$  in octahedral site that's way  $\text{Ni}^{2+}$

present in oh void.

Correct option is (d)

**14.Sol.** In  $\text{Fe}^{+2}\text{Fe}^{+3}_2\text{O}_4$  mixed oxide

→  $\text{Fe}^{+3}$  is  $d^5$  system with zero CFSE in octahedral void whereas  $\text{Fe}^{+2}$  is a  $d^6$  with  $-0.4 \Delta_0$  CFSE value in octahedral void so preferentially occupy octahedral site to give inverse spinel.

In  $\text{Co}^{+2}\text{Co}^{+3}_2\text{O}_4$  mixed oxide

$\text{Co}^{+3}$  is a  $d^6$  system with  $t_{2g}^6$  configuration in strong field octahedral  $\text{O}^{2-}$  voids to give max CFSE of  $-2.4 \Delta_0$  and hence this oxide is normal spinel.

Correct option is (d)

**15.Sol.**  $\text{Cr}^{3+}$  and  $\text{Co}^{3+}$  have high CFSE so prefer to remain in octahedral void and generally form normal spinel.  $\text{Al}^{3+}$  has high lattice energy due to which it remain in octahedral site and form normal spinel.

**16.Sol.** In normal spinel bivalent ion occupy tetrahedral site and trivalent ions occupy octahedral site as trivalent create more CFSE and are stable in octahedral void.

As oxides are weak field ligand therefore they prefer high spin configuration of metal ions.

So, option a, c are correct.

**17.Sol.**  $\text{Fe}_3\text{O}_4$  is a inverse spinel so it will exist as  $\text{Fe}^{2+}(\text{2Fe}^{3+})\text{O}_4$ . Here oxidation state is +2 as well as +3.

**18.Sol.**  $\text{Al}^{3+}$  has high lattice energy therefore form normal spinel with  $\text{Mg}^{2+}$  and  $\text{Co}^{2+}$  ions. But  $\text{Ni}^{2+}$  has large lattice energy as determined from lattice energy data and has high preference for octahedral site and form partial inverse spinel.

**9.Sol.**  $\% \text{ inverse character} = \frac{\lambda}{\lambda_{\text{max}}} \times 100 = \frac{\lambda}{0.5} \times 100 = 200\lambda$

As  $\lambda = 0.17$  (given)

$$\% \text{ inverse} = 200 \times 0.17 = 34\%$$

**20.Sol.** (3)  $\text{MnFe}_2\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$  and  $\text{NiAl}_2\text{O}_4$  are partial inverse spinel.

**21.Sol.**  $\text{MnAl}_2\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$  are normal spinels.





# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (11)

- Which of the following value of  $\lambda$  is not possible for any spinel.  
(a) zero (b) 0.45 (c) 1 (d) 0.5
- Which of the following metal ion generally from inverse spinel.  
(a)  $\text{Cr}^{3+}$  (b)  $\text{Co}^{3+}$  (c)  $\text{Fe}^{3+}$  (d)  $\text{Al}^{3+}$
- Which of the following is inverse spinel.  
(a)  $\text{ZnFe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4$  (c)  $\text{FeCr}_2\text{O}_4$  (d)  $\text{Mn}_3\text{O}_4$
- Which of the following is normal spinel.  
(a)  $\text{ZnFe}_2\text{O}_4$  (b)  $\text{NiGa}_2\text{O}_4$  (c)  $\text{CoFe}_2\text{O}_4$  (d)  $\text{FeFe}_2\text{O}_4$
- What is the value of  $\lambda$  for  $\text{ZnFe}_2\text{O}_4$   
(a) Zero (b) 0.5 (c) 0.9 (d) 1
- Calculate occupancy of  $\text{Fe}^{3+}$  ion in  $T_d$  void in a spinel  $\text{MnFe}_2\text{O}_4$  having  $\lambda = 0.15$
- For the spinel  $\text{ZnFe}_2\text{O}_4$  what is hybridisation of  $\text{Fe}^{3+}$  ion  
(a)  $\text{sp}^3$  (b)  $\text{sp}^3\text{d}^2$  (c)  $\text{d}^2\text{sp}^3$  (d)  $\text{sp}^3$  and  $\text{sp}^3\text{d}^2$  both
- The spinels  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  respectively are  
(a) Both inverse (b) Both normal (c) Inverse normal (d) Normal and inverse
- For the spinel  $\text{MnFe}_2\text{O}_4$  what is hybridisation of  $\text{Fe}^{3+}$  ion.  
(a)  $\text{sp}^3$  (b)  $\text{sp}^3$  (c)  $\text{d}^2\text{sp}^3$  (d)  $\text{sp}^3$  and  $\text{sp}^3\text{d}^2$  both
- $\text{Fe}^{3+}$  ions from normal spinel with which of the following ions.  
(a)  $\text{Mg}^{2+}$  (b)  $\text{Mn}^{2+}$  (c)  $\text{Zn}^{2+}$  (d)  $\text{Cu}^{2+}$
- What is the correct order of inverse character in spinel.  
(a)  $\text{Mn}_3\text{O}_4 < \text{MgFe}_2\text{O}_4 < \text{MnFe}_2\text{O}_4 < \text{NiAl}_2\text{O}_4 < \text{Mn}_3\text{O}_4$   
(b)  $\text{Mn}_3\text{O}_4 < \text{MnFe}_2\text{O}_4 < \text{NiAl}_2\text{O}_4 < \text{MgFe}_2\text{O}_4 < \text{Mn}_3\text{O}_4$   
(c)  $\text{Mn}_3\text{O}_4 < \text{NiAl}_2\text{O}_4 = \text{NiAl}_2\text{O}_4 = \text{MgFe}_2\text{O}_4 < \text{Mn}_3\text{O}_4$   
(d)  $\text{Mn}_3\text{O}_4 < \text{NiAl}_2\text{O}_4 < \text{MnFe}_2\text{O}_4 < \text{MgFe}_2\text{O}_4 < \text{Mn}_3\text{O}_4$

12. Which of the following shows normal spinel structure?  
 (a)  $\text{Fe}_3\text{O}_4$  (b)  $\text{Mn}_3\text{O}_4$  (c)  $\text{NiAl}_2\text{O}_4$  (d)  $\text{CuLa}_2\text{O}_4$
13. Among the compounds  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  and  $\text{Mn}_3\text{O}_4$   
 (a)  $\text{NiFe}_2\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  are normal spinels (b)  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  are normal spinels  
 (c)  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  are inverse spinels (d)  $\text{Fe}_3\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  are inverse spinels
14.  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$  are metal oxides having spinel structure. Considering their CFSE, the correct statement regarding their structure is  
 (a) both have normal spinel structure (b) both have inverse spinel structure  
 (c)  $\text{Fe}_3\text{O}_4$  has a normal and  $\text{Co}_3\text{O}_4$  are inverse spinels  
 (d)  $\text{Fe}_3\text{O}_4$  has a inverse and  $\text{Co}_3\text{O}_4$  are normal spinels
15. Which of the following metal ions generally form normal spinel.  
 (a)  $\text{Cr}^{3+}$  (b)  $\text{Co}^{3+}$  (c)  $\text{Fe}^{3+}$  (d)  $\text{Al}^{3+}$
16. Which of the following statements are true for spinel.  
 (a) In case of normal spinel bivalent ions occupy tetrahedral sites and trivalent ions occupy octahedral sites.  
 (b) In case of inverse spinel all bivalent cations are present in tetrahedral voids  
 (c) Since oxides ions are weak field ligands, the cation are found in high spin configurations.  
 (d) All of these
17. What is oxidation number of Fe in  $\text{Fe}_3\text{O}_4$   
 (a) +2 (b) +3 (c)  $8/3$  (d) zero
18.  $\text{Al}^{3+}$  ions from normal spinel with which of the following ions.  
 (a)  $\text{Mg}^{2+}$  (b)  $\text{Ni}^{2+}$  (c)  $\text{Co}^{2+}$  (d) All of these
19. For a given spinel  $\text{AB}_2\text{O}_4$ ,  $\lambda = 0.17$ . Calculate in what percent inversion take place.
20. How many from the following are partially inverse spinels.  
 $\text{MnFe}_2\text{O}_4$ ,  $\text{NiAl}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$
21. How many spinel from the following are normal?  
 $\text{MnAl}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$

## ANSWER KEY

- |     |           |     |        |     |        |     |        |     |     |     |     |     |     |
|-----|-----------|-----|--------|-----|--------|-----|--------|-----|-----|-----|-----|-----|-----|
| 1.  | (c)       | 2.  | (c)    | 3.  | (b)    | 4.  | (a)    | 5.  | (a) | 6.  | (0) | 7.  | (b) |
| 8.  | (a)       | 9.  | (d)    | 10. | (c)    | 11. | (b)    | 12. | (b) | 13. | (d) | 14. | (d) |
| 15. | (a, b, d) | 16. | (a, c) | 17. | (a, b) | 18. | (d, c) | 19. | 34% | 20. | 3   |     |     |
| 21. | 4         |     |        |     |        |     |        |     |     |     |     |     |     |

## HINTS & SOLUTION

- 1.Sol. As the value of  $\lambda$  lies between 0 to 0.5. So  $\lambda = 1$  not possible for any spinel.
- 2.Sol.  $\text{Fe}^{3+}$  ion has  $d^5$  configuration and form high spin complex. Therefore it will have zero CFSE. So, it will form inverse spinel.
- 3.Sol.  $\text{CoFe}_2\text{O}_4$  will form inverse spinel as  $\text{Co}^{2+}$  has large CFSE value.
- 4.Sol. As in  $\text{ZnFe}_2\text{O}_4$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$  both have zero CFSE and form normal spinel.
- 5.Sol.  $\text{ZnFe}_2\text{O}_4$  will form normal spinel so  $\lambda = 0$ .
- 6.Sol.  $\% \text{ inverse} = \frac{\lambda}{0.5} \times 100 = \frac{0.15}{0.5} \times 100 = 30\%$   
 $\text{T}_d \quad \text{O}_h$   
 In case of normal spinel  $\text{Mn}^{2+} \quad 2\text{Fe}^{3+}$   
 $\text{Fe}^{3+} = 0.3 \quad \text{Mn}^{2+} = 0.3$   
 When 30% inversion take place  $\text{Mn}^{2+} = 0.7 \quad \text{Fe}^{3+} = 1.7$   
 $\text{Fe}^{3+} \text{ in tetrahedral void} = \frac{0.3}{8} \times 100 = 3.75\%$
- 7.Sol. As the given spinel  $\text{ZnFe}_2\text{O}_4$  is normal. So,  $\text{Zn}^{2+}$  will lie in tetrahedral void and  $\text{Fe}^{3+}$  ions will lie in octahedral voids. So, hybridisation will be  $sp^3d^2$ .
- 8.Sol. As  $\text{Fe}^{3+}$  ion in both spinel have zero CFSE so, other ions  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  have more tendency to occupy octahedral site and will form inverse spinel.
- 9.Sol. As the given spinel is partial inverse spinel. So,  $\text{Fe}^{3+}$  will in octahedral as well as tetrahedral voids. In octahedral void its hybridisation will be  $sp^3d^2$  and in tetrahedral void hybridisation will be  $sp^3$ .
- 10.Sol.  $\text{Zn}^{2+}$  ion have zero CFSE so, it form normal spinel with  $\text{Fe}^{3+}$  ion.
- 11.Sol.  $\text{Fe}_3\text{O}_4 \quad \text{Mn}_3\text{O}_4 \quad \text{MnFe}_2\text{O}_4 \quad \text{NiAl}_2\text{O}_4 \quad \text{MgFe}_2\text{O}_4$   
 $\lambda = 0.5 \quad \lambda = 0 \quad \lambda = 0.1 \quad \lambda = 0.38 \quad \lambda = 0.45$

As in case of  $\text{MnFe}_2\text{O}_4$  both are transition element inverse character will be less. In case of  $\text{NiAl}_2\text{O}_4$  transition element Nickel is replacing  $\text{Al}^{3+}$ , a non transition element so inversion will not take place to much extend. But in case of  $\text{MgFe}_2\text{O}_4$   $\text{Mg}^{2+}$  which has high lattice energy can easily replace transition element. Therefore inversion will be more

So, correct option is (b)

- 12.Sol.  $\text{Mn}_3\text{O}_4$  will form normal spinel

- 13.Sol.  $\text{FeFe}_2\text{O}_4$  is inverse type spinel, because CFSE of  $\text{Fe}^{2+}$  is more than  $\text{Fe}^{3+}$  in octahedral site.

$\text{NiFe}_2\text{O}_4$  is also inverse type spinel. because CFSE of  $\text{Ni}^{2+}$  is more than  $\text{Fe}^{3+}$  in octahedral site that's way  $\text{Ni}^{2+}$

present in oh void.

Correct option is (d)

14.Sol. In  $\text{Fe}^{+2}\text{Fe}^{+3}_2\text{O}_4$  mixed oxide

→  $\text{Fe}^{+3}$  is  $d^5$  system with zero CFSE in octahedral void whereas  $\text{Fe}^{+2}$  is a  $d^6$  with  $-0.4 \Delta_0$  CFSE value in octahedral void so preferentially occupy octahedral site to give inverse spinel.

In  $\text{Co}^{+2}\text{Co}^{+3}_2\text{O}_4$  mixed oxide

$\text{Co}^{+3}$  is a  $d^6$  system with  $t_{2g}^6$  configuration in strong field octahedral  $\text{O}^{2-}$  voids to give max CFSE of  $-2.4 \Delta_0$  and hence this oxide is normal spinel.

Correct option is (d)

15.Sol.  $\text{Cr}^{3+}$  and  $\text{Co}^{3+}$  have high CFSE so prefer to remain in octahedral void and generally form normal spinel.  $\text{Al}^{3+}$  has high lattice energy due to which it remain in octahedral site and form normal spinel.

16.Sol. In normal spinel bivalent ion occupy tetrahedral site and trivalent ions occupy octahedral site as trivalent create more CFSE and are stable in octahedral void.

As oxides are weak field ligand therefore they prefer high spin configuration of metal ions.

So, option a, c are correct.

17.Sol.  $\text{Fe}_3\text{O}_4$  is a inverse spinel so it will exist as  $\text{Fe}^{2+}(\text{2Fe}^{3+})\text{O}_4$ . Here oxidation state is +2 as well as +3.

18.Sol.  $\text{Al}^{3+}$  has high lattice energy therefore form normal spinel with  $\text{Mg}^{2+}$  and  $\text{Co}^{2+}$  ions. But  $\text{Ni}^{2+}$  has large lattice energy as determined from lattice energy data and has high preference for octahedral site and form partial inverse spinel.

9.Sol.  $\% \text{ inverse character} = \frac{\lambda}{\lambda_{\text{max}}} \times 100 = \frac{\lambda}{0.5} \times 100 = 200\lambda$

As  $\lambda = 0.17$  (given)

$$\% \text{ inverse} = 200 \times 0.17 = 34\%$$

20.Sol. (3)  $\text{MnFe}_2\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$  and  $\text{NiAl}_2\text{O}_4$  are partial inverse spinel.

21.Sol.  $\text{MnAl}_2\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$  are normal spinels.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (12)

- The symmetry label of valence p orbitals of a metal ion in an octahedral ligand field is  
(a)  $t_{1g}$  (b)  $t_{2g}$  (c)  $e_g + a_{1g}$  (d)  $t_{2g}$
- The series with correct order of increasing  $\Delta_0$  in their complexes is  
(a)  $I^- < PR_3 < CH_3^- < CO$   
(b)  $PR_3 < CH_3^- < I^- < CO$   
(c)  $CH_3^- < PR_3 < I^- < CO$   
(d)  $I^- < CH_3^- < PR_3 < CO$
- The correct order of crystal field strength is : (Given: en = ethylenediamine)  
(a)  $Cl^- < H_2O < en < (\eta^5 - C_5H_5)^-$   
(b)  $H_2O < Cl^- < (\eta^5 - C_5H_5)^- < en$   
(c)  $H_2O < (\eta^5 - C_5H_5)^- < en < Cl^-$   
(d)  $en < Cl^- < H_2O < (\eta^5 - C_5H_5)^-$
- The ligand with only sigma ( $\sigma$ ) bonding character is  
(a)  $CN^-$  (b)  $CH_3^-$  (c) CO (d) NO
- Among  $(CH_3)_3P$ ,  $NO^+$ ,  $CN^-$  and  $I_3^-$ , the one which is not a  $\pi$ -acceptor ligand is—  
(a)  $I_3^-$  (b)  $CN^-$  (c)  $NO^+$  (d)  $(CH_3)_3P$
- As a ligand,  $Cl^-$  is—  
(a) Only  $\sigma$ -donor (b) Only  $\pi$ -donor  
(c) Both  $\sigma$ -donor and  $\pi$ -donor (d) A  $\sigma$ -donor and a  $\sigma$ -acceptor
- The ligand with only sigma ( $\sigma$ ) bonding character is—  
(a)  $CN^-$  (b)  $CH_3^-$  (c) CO (d) NO
- $d\pi-\sigma^*$  and  $d\pi-\pi^*$  types of donation of electrons from metal to ligand is shown by—  
(a)  $AsR_3$  (b)  $PR_3$  and halides (c)  $C = C$  and  $CN^-$  (d)  $AsR_3$  and  $SCN^-$

9. Which of the following ligands p $\pi$  - d $\pi$  interactions—  
 (a)  $\text{H}^-$  (b)  $\text{CH}_3^-$  (c)  $\text{RO}^-$  (d)  $\text{CR}_3^-$
10. The correct order of acceptor ability of the phosphines ligand is —  
 (a)  $\text{PMe}_3 > \text{PPh}_3 > \text{P(OPh)}_3 > \text{PF}_3$  (b)  $\text{PF}_3 > \text{P(OPh)}_3 > \text{PPh}_3 > \text{PMe}_3$   
 (c)  $\text{PF}_3 > \text{PMe}_3 > \text{PPh}_3 > \text{P(OPh)}_3$  (d)  $\text{P(OPh)}_3 > \text{PF}_3 > \text{PMe}_3 > \text{PPh}_3$
11. Among  $\text{RO}^-$ ,  $\text{AsMe}_3$ ,  $\text{ROR}'$ ,  $\text{CN}^-$ ,  $\text{RCO}_2^-$ ,  $\text{SCN}^-$ , the set of ligands with good  $\pi$ -acceptor nature are—  
 (a)  $\text{RO}^-$ ,  $\text{RCO}_2^-$ ,  $\text{SCN}^-$  (b)  $\text{RO}^-$ ,  $\text{RCO}_2^-$ ,  $\text{AsMe}_3$   
 (c)  $\text{AsMe}_3$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$  (d)  $\text{RO}^-$ ,  $\text{ROR}'$ ,  $\text{RCO}_2^-$
12. In transition metal nitrosyl ( $\text{M} - \text{NO}$ ) complexes, the back bonding involves donation of electrons from—  
 (a)  $\text{M} (t_{2g}) \rightarrow \text{NO}^+ (\sigma^*)$  (b)  $\text{M} (t_{2g}) \rightarrow \text{NO}^+ (\pi^*)$   
 (c)  $\text{M} (e_g) \rightarrow \text{N} (\pi)$  (d)  $\text{NO}^+ (\pi) \rightarrow \text{M} (t_{2g})$
13. Identify the order representing increasing  $\pi$ -acidity of the following compounds—  
 (a)  $\text{CN}^- < \text{C}_2\text{F}_4 < \text{NH}_3$  (b)  $\text{CN}^- > \text{C}_2\text{H}_4 > \text{C}_2\text{F}_4 > \text{NH}_3$   
 (c)  $\text{C}_2\text{H}_4 < \text{NH}_3 < \text{CN}^- < \text{C}_2\text{F}_4$  (d)  $\text{NH}_3 > \text{C}_2\text{H}_4 > \text{C}_2\text{F}_4 > \text{CN}^-$
14. The order of reactivity of ligands,  $\text{NMe}_3$ ,  $\text{PMe}_3$  and  $\text{CO}$  with complexes  $\text{MeTiCl}_3$  and  $(\text{CO})_5\text{Mo}(\text{THF})$  are—  
 (a)  $\text{CO} > \text{PMe}_3 > \text{NMe}_3$  for  $\text{MeTiCl}_3$  (b)  $\text{CO} > \text{PMe}_3 > \text{NMe}_3$  for  $(\text{CO})_5\text{Mo}(\text{THF})$   
 (c)  $\text{NMe}_3 > \text{PMe}_3 > \text{CO}$  for  $\text{MeTiCl}_3$  (d)  $\text{NMe}_3 > \text{PMe}_3 > \text{CO}$  for  $(\text{CO})_5\text{Mo}(\text{THF})$
15. Among the following options, which statements are incorrect—  
 (a)  $\text{C}_2\text{F}_4$  is a  $\pi$ -acceptor ligand  
 (b)  $\pi$ -acidity order is  $\text{NMe}_3 > \text{PMe}_3 > \text{CO}$   
 (c) High oxidation state of metal is favourable for attack of  $\pi$ -acceptor ligands  
 (d) d $\pi$ - $\pi^*$  type of donation is observed  $\text{PMe}_3$ ,  $\text{CO}$  and  $\text{CN}^-$
16. According to LFT, the correct statements are—  
 (a) Ligands which has higher  $\Delta_o$  are generally  $\pi$ -acceptor ligands.

(b)  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals are not involved in construction of LGOs.

(c) Back donation in  $(M-PR_3)$  metal phosphine complexes involves  $M(t_{2g}) \rightarrow PR_3(\sigma^*)$

(d) Spectrochemical series can be easily explained by LFT.

17. How many of the following ligands can behave as  $\pi$ -acids?

$NR_3$ ,  $PMe_3$ ,  $CO$ ,  $CN^-$ ,  $C_2H_4$ ,  $CH_3^-$ ,  $OH_2$ ,  $I^-$ ,  $NO^+$ ,  $C_2F_4$

18. Number of ligands which are preferable for the attack on  $Mo(CO)_5(thf)$  like complexes—

$CN^-$ ,  $I_3^-$ ,  $OH_2$ ,  $NEt_3$ ,  $PF_3$ ,  $F^-$ ,  $Co$

## ANSWER KEY

- |     |         |     |           |     |     |     |     |     |     |     |     |     |       |
|-----|---------|-----|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|
| 1.  | (b)     | 2.  | (d)       | 3.  | (a) | 4.  | (b) | 5.  | (a) | 6.  | (c) | 7.  | (b)   |
| 8.  | (d)     | 9.  | (c)       | 10. | (b) | 11. | (c) | 12. | (b) | 13. | (d) | 14. | (a,c) |
| 15. | (b,c,d) | 16. | (a,b,c,d) | 17. | 6   | 18. | 3   |     |     |     |     |     |       |

## HINTS & SOLUTION

**1Sol.** The symmetry of label of valence P orbital of a metal ion in an octahedral ligand field is  $t_{1u}$ .

Correct option is (b)

**2Sol.** Increasing  $\Delta_0$  depends on strength of ligands as we know sequence of ligands in spectrochemical series takes form :  $\pi$  donor < only  $\sigma$  donor <  $\pi$  acceptor.

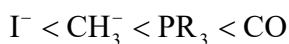
CO and  $PR_3$  are  $\pi$  acceptor

$CH_3^-$  is only  $\sigma$  donor

$I^-$  is  $\pi$  donor

as CO accepts in low lying  $\pi^*$  orbital while  $PR_3$  accepts in relatively high energy  $\sigma^*$  orbital therefore CO is relatively more stronger than  $PR_3$ .

So correct order of ligands with their increasing tendency to influence  $\Delta_0$  is

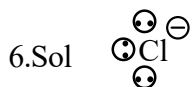


Correct option is (d)

**3Sol.** Correct option is (a)

**4Sol.** Correct answer is (b)

**5Sol.**  $I_3^-$  is a  $\sigma$  donor ligand while  $CN^-$ ,  $NO^+$  and  $(CH_3)_3P$  are  $\pi$ -acceptor ligands.



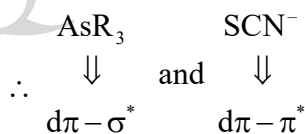
$\Rightarrow$  It can form  $\sigma$  bond with metal from negative charge and then can further donate using its lone pairs.



**7Sol.**  $CH_3^+$  is a  $\sigma$ -bonding ligand while,  $CN^-$ , CO, NO are  $\pi$ -acceptor ligands.

**8Sol.**  $d\pi-\sigma^* \Rightarrow$  ligand accepts  $e^-$  density from metal in vacant  $\sigma^*$  orbitals

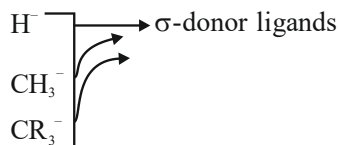
$d\pi-\pi^* \Rightarrow$  ligand accepts  $e^-$  density from metal to vacant  $\pi^*$  orbitals



Both ligands are  $\pi$ -acceptor in nature though.

**9Sol.** Only  $\pi$ -donor ligands shows  $p\pi - d\pi$  type interactions

$\therefore RO^-$  is capable of such interaction.

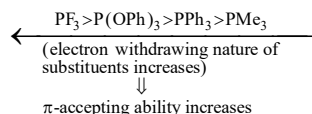


**10Sol.** Lesser the electron density on donor atom or more deficient the donor atom, greater will be  $\pi$ -accepting ability.



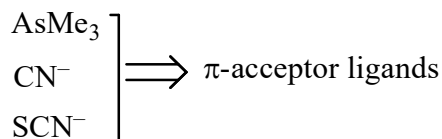
When electron withdrawing groups attached to donor atom,  $\pi$ -accepting tendency increases.

Electron donating groups decreases the accepting ability.



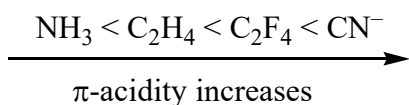
11.Sol.  $\text{RO}^- \Rightarrow \pi$ -donor ligand

$\text{ROR}' \Rightarrow \sigma$ -donor ligand



12.Sol.  $\text{NO}^+$  is a  $\pi$ -acceptor ligand. So, after donation from  $\sigma$ -bond, it will accept  $e^-$  density from metal [as  $\text{M}(t_{2g}) \rightarrow \text{NO}^+(\pi^*)$  in its  $\pi^*$  orbital].

13.Sol.  $\pi$ -acidity means  $\pi$ -accepting character



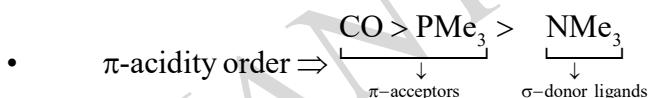
14.Sol.  $\text{MeTiCl}_3$ , in this complex, Ti is in +4 oxidation state. Therefore, it reacts faster with  $\sigma$ -donor ligands.

$\text{NMe}_3 > \text{PMe}_3 > \text{CO}$

$(\text{CO})_5\text{Mo}(\text{THF})$ , Mo is in low oxidation state, hence reacts faster with  $\pi$ -acceptor ligands

$\text{CO} > \text{PMe}_3 > \text{NMe}_3$

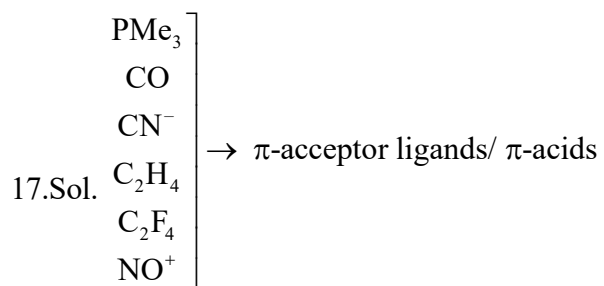
15.Sol.



- $\pi$ -acidity order  $\Rightarrow$   $\text{CO} > \text{PMe}_3 > \text{NMe}_3$
- High oxidation state of metal favours attack of  $\pi$ -donor or  $\sigma$ -donor ligands
- $d\pi\text{-}\pi^*$  type of donation is observed CO and  $\text{CN}^-$  while in  $\text{PMe}_3$  it is of  $d\pi\text{-}\sigma^*$  type.

16.Sol.

- $\pi$ -acceptor ligands have higher  $\Delta_o$  values because these involves transition of electrons from  $(t_{2g}) \rightarrow (e_g^*)$
- ligand approach axially and  $d_{xy}, d_{yz}, d_{xz}$  orbitals are non-axial therefore, not involved in construction of LGOs.
- $(\text{M} - \text{PR}_3)$  complexes, back donation is form  $\text{M}(t_{2g})$  to  $\text{PR}_3(\sigma^*)$
- Spectrochemical series involves WFL on left & SFL on right side which can be explained by LFT as  $\pi$ -acceptor ligands are generally SFL and  $\pi$ -donor ligands are WFL while those in middle are sigma donors.



18.Sol.  $\text{Mo(CO)}_5$  (thf), Mo is in low oxidation state, so,  $\pi$ -acceptor ligands will be preferable for attack.  
 $\therefore \text{CN}^-$ ,  $\text{PF}_3$  & CO will be favoured.




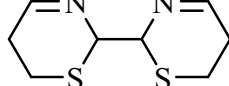
# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (13)

- Which of the following complexes does not form tetrahedral geometry?  
(a)  $[\text{CuBr}_4]^{2-}$  (b)  $[\text{RhCl}_2(\text{PPh}_3)_2]$  (c)  $[\text{MnO}_4]^-$  (d)  $[\text{FeCl}_4]^{2-}$
- Hybridization which does not involved in trigonal prismatic?  
(a)  $\text{pd}^5$  (b)  $\text{sd}^5$  (c)  $\text{spd}^4$  (d)  $\text{d}^2\text{sp}^3$
- Consider the coordination compound  $\text{K}_2[\text{Cu}(\text{CN})_4]$ . A coordinate covalent bond exists between  
(a)  $\text{K}^+$  and  $\text{CN}^-$  (b)  $\text{Cu}^{2+}$  and  $\text{CN}^-$  (c)  $\text{K}^+$  and  $[\text{Cu}(\text{CN})_4]^{2-}$  (d)  $\text{K}^+$  and  $\text{Cu}^{2+}$
- The geometry of  $[\text{Co}(\text{CN})_4]^{2-}$  is  
(a) tetrahedral (b) square planar (c) square pyramidal (d) none of these
- What is the hybridisation and geometry of  $\text{Re}(\text{CH}_3)_6$ ?  
(a)  $\text{d}^4\text{sp}$ , trigonal prismatic (b)  $\text{pd}^5$ , trigonal prismatic  
(c)  $\text{p}^3\text{d}^3$ , octahedral (d)  $\text{sp}^3\text{d}^2$ , octahedral
- Aluminium chloride in acidified aqueous solution forms a complex 'A' in which hybridisation of Al is 'B'. What are 'A' and 'B' respectively?  
(a)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ,  $\text{sp}^3\text{d}^2$  (b)  $[\text{Al}(\text{H}_2\text{O})_4]^{3+}$ ,  $\text{sp}^3$   
(c)  $[\text{Al}(\text{H}_2\text{O})_4]^{3+}$ ,  $\text{dsp}^2$  (d)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ,  $\text{d}^2\text{sp}^3$
- What is the coordination number of  $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$  and  $[\text{Cu}(\text{bipy})_2]\text{I}$   
(a) 6, 5 (b) 2, 3 (c) 4, 4 (d) 3, 5
- The d-orbitals which participate in  $\text{d}^2\text{sp}^3$  or  $\text{sp}^3\text{d}^2$ -hybridization are:  
(a)  $\text{d}_{xy}$ ,  $\text{d}_{yz}$  (b)  $\text{d}_{x^2-y^2}$ ,  $\text{d}_{z^2}$  (c)  $\text{d}_{xz}$ ,  $\text{d}_{yz}$  (d)  $\text{d}_{x^2-y^2}$ ,  $\text{d}_{xy}$
- The structure of the complexes  $[\text{Mn}(\text{acac})_2\text{bpy}]$  and  $\text{CrO}(\text{O}_2)_2(\text{Py})$  respectively are  
(a) Square pyramidal and octahedral  
(b) trigonal prismatic and octahedral  
(c) trigonal bipyramidal and octahedral  
(d) trigonal prismatic and pentagonal pyramidal

10. The structure of the complexes  $\text{Fe}(\text{BHX}_3)_3$  and  $[\text{Fe}(\text{btz})_2(\text{NCS}-\text{N})_2]$  respectively are  
 $\text{X} : \longrightarrow$   and  $\text{btz} : \longrightarrow$  
- (a) Linear and octahedral (b) square planar and octahedral  
 (c) square pyramidal and square planar (d) octahedral and octahedral
11. The structures of  $\text{FeO}_4^{4-}$  and  $\text{OsO}_5^{2-}$  respectively are  
 (a) tetrahedral and trigonal bipyramidal  
 (b) tetrahedral and square pyramidal  
 (c) square planar and trigonal bipyramidal  
 (d) distorted tetrahedral and trigonal bipyramidal.
12. What is the coordination number of the complex  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$  is  
 (a) 5 (b) 6 (c) 7 (d) 12
13. In trigonal prismatic ligand, the most stabilized d-orbital is  
 (a)  $d_{z^2}$  (b)  $d_{xy}$  (c)  $d_{xz}$  (d)  $d_{yz}$
14. Which geometry is not consistent with a coordination number 8?  
 (a) Dodecahedral (b) Square antiprismatic  
 (c) Hexagonal pyramidal (d) Bicapped trigonal prismatic
15. Which of the following statement is correct.  
 (a) The energy difference between square antiprismatic and do-decahedral structures for  $[\text{W}(\text{CN})_8]^{3-}$  is small  
 (b) 9-coordinate structures are common for first row d-block metal ions  
 (c) 4-coordinate complexes of  $\text{Co}(\text{II})$  are always square planar.  
 (d) All of these
16. Which of the following is an example of a trigonal prismatic complex?  
 (a)  $[\text{ZrMe}_6]^{2-}$  (b)  $[\text{Mn}(\text{CN})_6]^{3-}$  (c)  $[\text{Cu}(\text{NO}_2)_6]^{4-}$  (d)  $[\text{VF}_6]^{2-}$
17. Geometry shown by  $[\text{Ni}(\text{CN})_5]^{3-}$   
 (a) trigonal bipyramidal (b) square pyramidal  
 (c) pentagonal bipyramidal (d) none of these

18. Which of the following statements are correct?

- (a)  $[\text{Ag}(\text{NH}_3)_2]^+$  is linear with sp hybridised  $\text{Ag}^+$  ion.  
 (b)  $\text{NiCl}_4^{2-}$ ,  $\text{VO}_4^{3-}$  and  $\text{MnO}_4^-$  have tetrahedral geometry.  
 (c)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  have  $\text{dsp}^2$  hybridisation of the metal ions.  
 (d) None of these

19. How many of following complexes shows distortion from tetrahedral geometry?

$\text{CoCl}_4^{2-}$ ,  $[\text{NiCl}_2(\text{PPh}_3)_2]$ ,  $\text{Cs}_2[\text{CuCl}_4]$ ,  $\text{NiCl}_4^{2-}$ ,  $(\text{NMe}_4)_2\text{CuCl}_4$ ,  $[\text{RhCl}(\text{PPh}_3)_3]$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{NiCl}_2(\text{PMe}_3)_2]$ .

20. From the following how many complexes form trigonal prismatic geometry.

$\text{Re}(\text{CH}_3)_6$ ,  $\text{WSe}_2$ ,  $\text{Zr}(\text{CH}_3)_6^{2-}$ ,  $[\text{Mo}(\text{S} - \text{C} = \text{C} - \text{S})_3]$ ,  $\text{ZrS}_2$ ,  $\text{TaS}_2$ ,  $\text{TaSe}_2$ ,  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{V}(\text{NH}_3)_6^{2+}$ .

21. Which of the following complexes are shown tetragonally distortion?

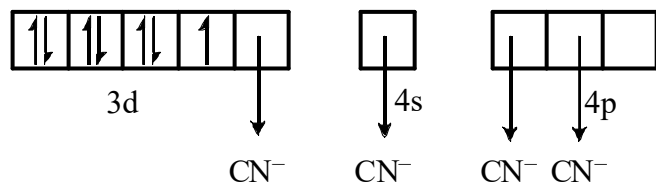
$[\text{Mn}(\text{CN})_6]^{3-}$ ,  $\text{TiF}_6^{2-}$ ,  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$ ,  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Cu}(\text{NO}_2)_6]^{4-}$

## ANSWER KEY

1.	(b)	2.	(d)	3.	(b)	4.	(b)	5.	(a)	6.	(a)	7.	(a)
8.	(b)	9.	(d)	10.	(c)	11.	(d)	12.	(b)	13.	(b)	14.	(c)
15.	(a)	16.	(a)	17.	(a,b)	18.	(a, b, c)	19.	2	20.	6	21.	4

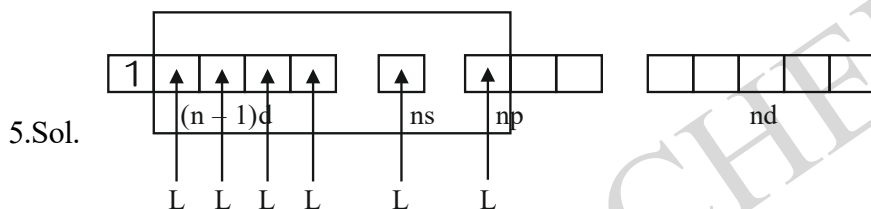
## HINTS & SOLUTION

- 1.Sol. Option (b) does show square planar geometry it do not show tetrahedral geometry due to steric repulsion between  $\text{PPh}_3$  ligand in this  $\text{Rh}(+1) \rightarrow d^8 \rightarrow$  Complexes form square planar geometry.
- 2.Sol.  $d^2sp^3$  hybridization involved in octahedral geometry so option (d) is correct.
- 3.Sol. Option (b) is correct  $\text{Cu}^{2+}$  and  $\text{CN}^-$  does have coordination bond which is formed in between metal and ligand.
- 4.Sol.  $\text{Co}^{2+} \rightarrow 3d^7$   $\text{CN}^- \rightarrow$  Strong field ligand (Low spin)



hybridisation  $\rightarrow dsp^2$  (Square planar)

So option (b) is correct.

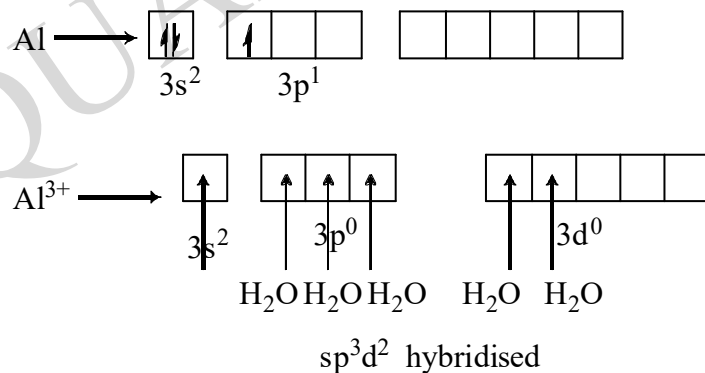
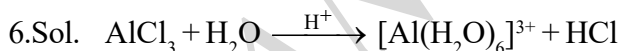


$\text{Re}(\text{CH}_3)_6 \rightarrow d^5s^2$

$\text{Re}^{+6} \rightarrow d^1$

Hybridisation is  $d^4sp$  and geometry is trigonal prismatic.

Correct option is (a)



- 7.Sol. In  $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$  there are  $2\text{NH}_3$ ,  $4\text{NCS}$  are bonded to central metal cation in the complex there coordination number of the central metal cation is 6.

In  $[\text{Cu}(\text{bipy})_2]\text{I}$  there are  $2\text{bipy}$  and  $1\text{I}$  bonded to central metal cation in the complex. Therefore the coordination number of central metal cation is 5.

So option (a) is correct.

- 8.Sol. The d-orbitals which lies on axes participate in  $d^2sp^3$  or  $sp^3d^2$  hybridisation. So  $d_{x^2-y^2}$  and  $d_{z^2}$  participate in

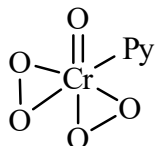
$d^2sp^3$  or  $sp^3d^2$  hybridisation.

9.Sol.  $Mn(acac)_2 \cdot bpy$

↓  
Coordination no. of Mn is = 6

$Mn^{2+} \rightarrow d^5 \rightarrow HS$

if form trigonal prismatic structure because its bite angle is low.



Structure of  $Cr(O_2)_2OPy$ .

Pentagonal pyramidal

Correct option is (d)

10.Sol.  $Fe[BHX_3]_2 \rightarrow CN = 5 \rightarrow$  square pyramidal

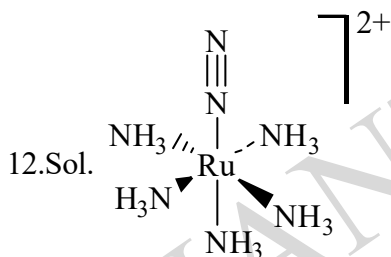
$[Fe(btz)_2(NCS-N)_2] \rightarrow CN = 4 \rightarrow$  square planar.

11.Sol.  $FeO_4^{4-} \rightarrow Fe^{+4} \rightarrow d^4$  shows distorted tetrahedral due to Jahn-teller-distortion.

$OsO_5^{2-} \rightarrow Os \rightarrow +8$

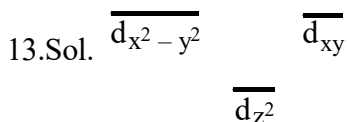
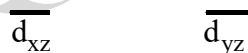
Osmium is coordinated by five oxygen atoms which are forming a trigonal bipyramidal.

Correct option is (d).



Coordination number of  $Ru^{2+}$  is 6.

So option (b) is correct.

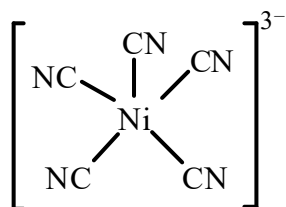


trigonal prismatic

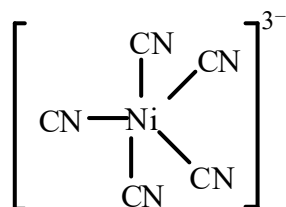
in trigonal prismatic ligand the most stabilized d-orbital is  $d_{z^2}$

So option (a) is correct.

- 14.Sol.** Geometry associated with coordination number 8 are bicapped trigonal prismatic, cubic, hexagonal bipyramidal.
- 15.Sol.** EPR spectra of  $[\text{W}(\text{CN})_8]^{3-}$  reveals that  $[\text{W}(\text{CN})_8]^{3-}$  can exist in both geometry square antiprismatic and dodecahedral structure and difference between energy is small.
- 16.Sol.**  $[\text{ZrMe}_6]^{2-}$  form trigonal prismatic complex other all are octahedral.
- 17.Sol.** Option (a) and (b) both are correct.  $[\text{Ni}(\text{CN})_5]^{3-}$  ion can exist as both square pyramidal and trigonal bipyramidal in the same crystal.



Square pyramidal



Trigonal bipyramidal

- 18. Sol.**(a)  $[\text{Ag}(\text{NH}_3)_2]^+$  is linear with  $sp$  hybridised  $\text{Ag}^+$  ion.
- (b)  $\text{NiCl}_4^{2-}$ ,  $\text{VO}_4^{3-}$  have tetrahedral geometry because they are  $sp^3$  hybridised.
- (c)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are  $dsp^2$  hybridised to metal ion, because  $\text{NH}_3$  and  $\text{CN}^-$  are strong field ligand.

Correct option is a, b, c

- 19. Sol.**  $\text{Cs}_2[\text{CuCl}_4]$  and  $(\text{NMe}_4)_2\text{CuCl}_4$  show distorted tetrahedral geometry due to Jahn teller effect in which two of the  $\text{Cl}-\text{Cu}-\text{Cl}$  bond angles  $102^\circ$  and two near  $125^\circ$ .
- 20. Sol.** Those have  $d^0/d^1$  configuration with bulky organic ligand ( $\text{R} \rightarrow \text{CH}_3$ ) form trigonal prismatic geometry and having lattice packing (radius ratio)  $r^+/r^-$  is greater than 1.8 form trigonal prismatic geometry.

$\text{Re}(\text{CH}_3)_6$ ,  $\text{WSe}_2$ ,  $\text{Zr}(\text{CH}_3)_6^{2-}$ ,  $[\text{Mo}(\text{S}-\text{C}=\text{C}-\text{S})_3]$ ,  $\text{TaSe}_2$ ,  $\text{MoS}_2$  form trigonal prismatic geometry.

- 21. Sol.**  $[\text{Mn}(\text{CN})_6]^{3-} \rightarrow d^4 \rightarrow t_{2g}^4 \rightarrow \text{yes}$

$\text{TiF}_6^{2-} \rightarrow d^0 \rightarrow \text{no}$

$[\text{Mn}(\text{H}_2\text{O})_6]^{2+} \rightarrow d^5 \rightarrow t_{2g}^3 e_g^2 \rightarrow \text{no}$

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \rightarrow d^6 \rightarrow t_{2g}^4 e_g^2 \rightarrow \text{yes}$

$[\text{Fe}(\text{CN})_6]^{3-} \rightarrow d^5 \rightarrow t_{2g}^5 \rightarrow \text{yes}$

$[\text{Cr}(\text{CN})_6]^{3-} \rightarrow d^3 \rightarrow t_{2g}^3 e_g^0 \rightarrow \text{no}$

$[\text{Zn}(\text{H}_2\text{O})_6]^{2+} \rightarrow d^{10} \rightarrow t_{2g}^6 e_g^4 \rightarrow \text{no}$

$[\text{Cu}(\text{NO}_2)_6]^{4+} \rightarrow d^9 \rightarrow t_{2g}^6 e_g^3 \rightarrow \text{yes}.$

$[\text{Mn}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Cu}(\text{NO}_2)_6]^{4+}$ . This complexes show jahn-teller-distortions.





# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (14)

- Which of the following statement is not true on the basis of Jahn Teller Distortion.
  - Ligandogenerated distortions can be different along all direction.
  - Metallogenerated distortions lower the symmetry of complex to some extent.
  - Ligandogenerated distortions are not responsible for colour of complex.
  - Metallogenerated distortions are responsible for colour of complex.
- Jahn-Teller Theorem is not applicable to —
  - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
  - $\text{FeO}_4^{4-}$
  - $\text{Cu}(\text{CN})_5^{3-}$
  - $[\text{Ag}(\text{NH}_3)_2]^+$
- What is the correct order of extend of JTD.
  - Octahedral > Tetrahedral > Square pyramidal
  - Square pyramidal > Octahedral > Tetrahedral
  - Octahedral > Square pyramidal > Tetrahedral
  - Octahedral > Square planar > Tetrahedral
- For which configuration in all the set of d-electrons JTD is not possible ?
  - $d^2, d^9, d^7, d^5(\text{HS}), d^1$
  - $d^3, d^8, d^{10}, d^5(\text{HS}), d^6(\text{LS})$
  - $d^3, d^8, d^7, d^1, d^2$
  - $d^{10}, d^9, d^6(\text{LS}), d^5, (\text{HS}), d^1$
- Jahn-teller effect is not observed in high spin complexes of —
  - $\text{Mn}^{2+}$
  - $\text{Cr}^{2+}$
  - $\text{Cu}^{2+}$
  - $\text{Fe}^{2+}$
- Which of the following will show strong Jahn-teller distortion ?
  - $\text{Fe}^{3+}$
  - High Spin  $\text{Co}^{2+}$
  - $\text{Ti}^{2+}$
  - Low spin  $\text{Co}^{2+}$
- Which of the following d-configuration shows strong distortion from octahedral geometry ?
  - $d^1$
  - $d^2$
  - $d^9$
  - None
- Which metal complex ion is expected to be subject to a Jahn-teller distortion?
  - $\text{Cu}^{2+}$
  - $\text{Ni}^{2+}$
  - $\text{Ca}^{2+}$
  - $\text{Cr}^{3+}$

9. Which metal complex ion is expected to be subjected to a Jahn-Teller distortion ?  
 (a)  $[\text{Cr}(\text{OH}_2)_6]^{3+}$  (b)  $[\text{Cr}(\text{NH}_3)_6]^{2+}$  (c)  $[\text{Cr}(\text{CN})_6]^{3-}$  (d)  $[\text{Cr}(\text{bpy})_3]^{3+}$
10. The true statements about  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is  
 (a) All Cu – O bond length are equal  
 (b) One Cu – O bond length is shorter than remaining five.  
 (c) Three Cu – O bond lengths are shorter than the remaining three.  
 (d) Four Cu – O bond lengths are shorter than the remaining two.
11. Among the following the complex ion that would show strong Jahn-Teller Distortion is  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  (b)  $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$  (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
12. Strong Jahn-teller distortion is not observed for octahedral complexes of  
 (a)  $\text{Cu}^{2+}$  (b) Low spin  $\text{Cr}^{2+}$  (c) High spin  $\text{Mn}^{3+}$  (d) High spin  $\text{Cr}^{2+}$
13. The extra stability of  $\text{Cu}(\text{II})$  ion is due to —  
 (a) Jahn-teller distortion (b) Compton effect  
 (c) Square planar geometry (d) CFSE
14. Which of the following pairs of electronic configuration of high-spin transition metal ions (3d) in an octahedral field undergo a substantial Jahn-teller distortion.  
 (a)  $d^3, d^9$  (b)  $d^4, d^9$  (c)  $d^5, d^9$  (d)  $d^6, d^9$
15. The set of ions expected to show Jahn-Teller distortion in their complexes is  
 (a)  $\text{Ti}(\text{III})$ ,  $\text{Cu}(\text{II})$ , high spin  $\text{Fe}(\text{III})$  (b)  $\text{Cu}(\text{I})$ ,  $\text{Ni}(\text{II})$ , High spin  $\text{Fe}(\text{III})$   
 (c)  $\text{Cu}(\text{II})$ , Low spin  $\text{Fe}(\text{III})$ ,  $\text{Ti}(\text{III})$  (d) Low spin  $\text{Fe}(\text{III})$ ,  $\text{Mn}(\text{II})$ ,  $\text{Cu}(\text{I})$
16. The correct statement for Mn–O bond lengths in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  is  
 (a) All bonds are equal  
 (b) Four bonds are longer than two others  
 (c) Two bonds are longer than four others  
 (d) They are shorter than the Mn–O bond in  $[\text{MnO}_4]^-$
17. Which of the following statements is / are true on the basis of Jahn-Teller Distortion.  
 (a) It explain qualitative aspects of distortion  
 (b) It explain quantative aspects of distortion  
 (c) Thermodynamic stability of complex increases due to Jahn-Teller distortion.  
 (d) First order Jahn-Teller distortion are considered as weak distortion.

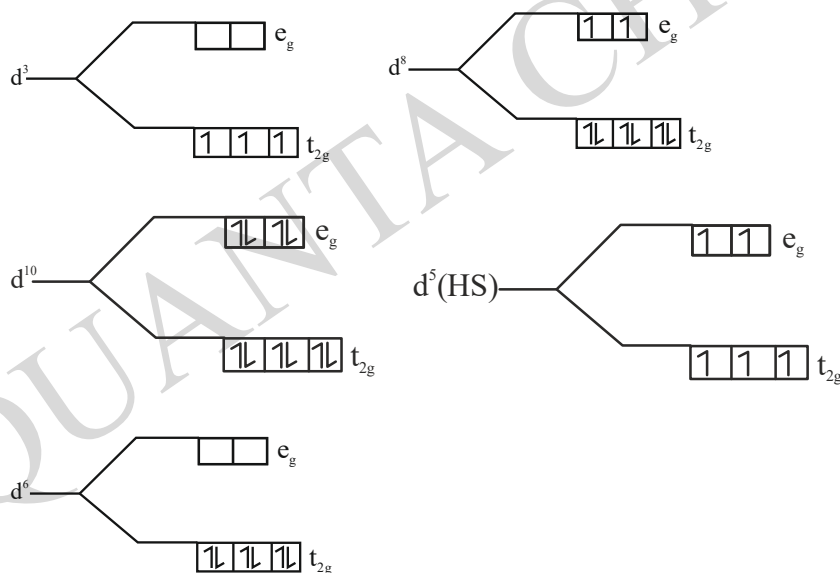
18. Which of the following statements are correct?
- If  $CFSE = 0$  then JTSE is also zero
  - If JTSE is zero then CFSE is also zero
  - All compounds which have ( $CFSE = 0$ ) doesn't show JTD
  - Compounds having  $CFSE = 0$  may show PJTD
19. Which of the following statements are true for Jahn-Teller Distortion:
- For ' $Z_{in}$ ' distortion, the splitting pattern is similar to that observed for ' $Z_{out}$ ', but the energy order within  $e_g$  and  $t_{2g}$  level is inverted.
  - Octahedral complex [ $d^9$ ,  $d^4(HS)$ ] undergo large splittings due to strong first order Jahn-Teller effect.
  - Distortion effects are expected to be less pronounced in  $t_{2g}$  orbital because  $t_{2g}$  level is much more involved in a bonding than  $e_g$ .
  - Six – coordinated manganese (III) complexes can be readily interpreted in term of compression along the z-axis.
20. How many configuration from the following are in Electronically degenerate state,  $p^4$ ,  $d^3$  (Isolated state),  $d^3$  (Octahedral field),  $d^5$  (Isolated state)

### ANSWER KEY

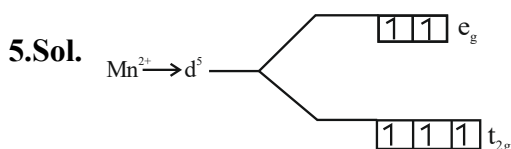
- |         |         |            |               |            |         |         |
|---------|---------|------------|---------------|------------|---------|---------|
| 1. (c)  | 2. (d)  | 3. (c)     | 4. (b)        | 5. (a)     | 6. (d)  | 7. (c)  |
| 8. (a)  | 9. (b)  | 10. (d)    | 11. (a)       | 12. (b)    | 13. (a) | 14. (b) |
| 15. (c) | 16. (a) | 17. (c, d) | 18. (a, c, d) | 19. (a, b) | 20. (2) |         |

## HINTS & SOLUTION

- 1.Sol.** Ligandgenerated distortions also contribute for colour of complex as due to Assymetric ligand relaxation Laporte forbidden transitions are relaxed.
- 2.Sol.** Here  $[\text{Ag}(\text{NH}_3)_2]^+$  has linear arrangement. But according to statement of Jahn-Teller Theorem it is applicable to non-linear system which have electronically degenerate state. Jahn-Teller Distortions are not observed in  $[\text{Ag}(\text{NH}_3)_2]^+$  complex.
- 3.Sol.** Extend of JTD  $\propto$  (Z-content in hybridization)
- Octahedral  $\rightarrow S + P_x + P_y + P_z + d_{z^2} + d_{x^2-y^2}$
- Square pyramidal  $\rightarrow S + P_x + P_y + P_z + d_{x^2-y^2}$
- Tetrahedral  $\rightarrow S + P_x + P_y + P_z$
- So, Correct option is (c)
- 4.Sol.** No distortion  $\rightarrow$  Complex is electronically non-degenerate  
 Slight distortion  $\rightarrow$  Complex is electronically triply degenerate.  
 Strong distortion  $\rightarrow$  Complex is electronically doubly degenerate.



Option (b) is correct.

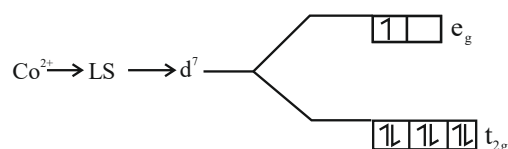


$\text{Mn}^{2+}$  complexes are electronically non degenerate.

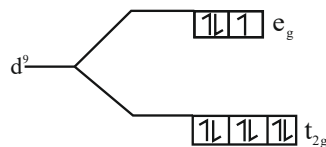
So the complexes of  $\text{Mn}^{2+}$  JTD does not occur.

Option (a) is correct.

6.Sol.



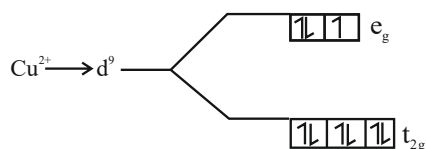
In  $\text{Co}^{2+}$  shows strong JTD because here  $e_g$  orbitals are unsymmetrically filled.

7.Sol.  $d^9$  complexes show strong JTD because in this  $e_g$  orbitals are unsymmetrically filled.

Option (c) is correct.

Correct option is (d).

8.Sol.

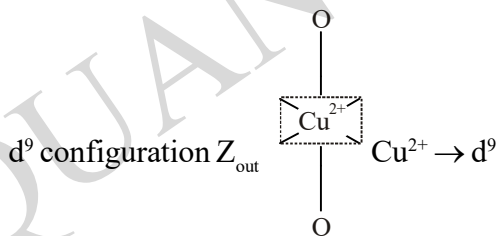


When  $t_{2g}$  or  $e_g$  orbitals are unsymmetrically filled then distortion occur, more distortion occurs when  $e_g$  orbital are electronically degenerate because this  $e_g$  orbitals point directly towards the ligands & more repulsion will occur.

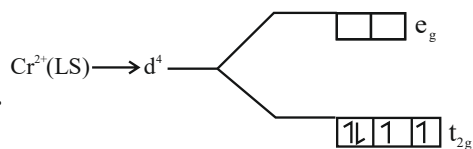
Correct option (a).

9.Sol. In complex  $[\text{Cr}(\text{NH}_3)_6]^{2+}$ , Cr has  $t_{2g}^3 e_g^1$  configuration. As  $e_g$  is unsymmetrically filled so, will under go Jahn Teller distortion.

10.Sol. (d) Due to JTD

11.Sol. In complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  the electronic configuration of  $\text{Cr}^{2+}$  is  $t_{2g}^3 e_g^1$  as  $e_g$  is unsymmetrically filled so Jahn Teller distortions will be observed in the complex. Distortions are more in case when  $e_g$  is unsymmetrically filled in comparison to  $t_{2g}$ .

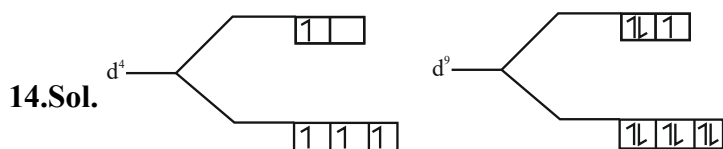
12.Sol.



In  $\text{Cr}^{2+}(\text{LS})$  complex strong JTD is not observed because in these  $t_{2g}$  orbitals are unsymmetrically filled. Strong distortion occur in the complex when  $e_g$  orbitals are unsymmetrically filled.

13.Sol. The extra stability of Cu (II) ion can be explained by taking into account of Jahn-Teller distortion of this  $d^9$  ion.

Option (a) is correct.



In  $d^4$ ,  $d^9$   $e_g$  orbitals are electronically degenerate state. So it will show Jahn-teller distortion.

Correct option is (b).

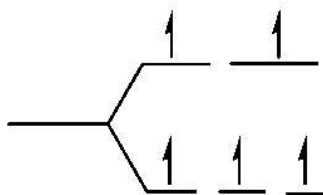
15.Sol.  $\text{Cu}^{2+} \rightarrow t_{2g}^6 e_g^3$  unsymmetrically filled  $e_g$

$\text{Fe}^{3+}$  low spin  $\rightarrow t_{2g}^5 e_g^0 \rightarrow$  unsymmetrically filled  $t_{2g}$

$\text{Ti(III)} \rightarrow t_{2g}^1 e_g^0 \rightarrow$  unsymmetrically filled  $t_{2g}$ .

Correct option is (c)

16.Sol.  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} = d^5 (\text{H.S})$



As all the levels are electronically non-degenerate. Hence, No Jahn-Teller distortion. Therefore, all the Mn-O bond length will be equal.

Correct option is (a)

17.Sol. Jahn-Teller distortion does not explain quantitative & qualitative aspects of distortion. Jahn-Teller distortion is one of the factor to explain thermodynamic stability.

18.Sol. For a complex  $d^5(\text{HS})$  CFSE = 0 and no JTd is observed therefore JTSE is also zero.

All compounds which have zero CFSE may show pseudo Jahn Teller Distortion.

19.Sol. Distortion effects are expected to be less pronounced in  $t_{2g}$  orbital because  $t_{2g}$  level is less involved in bonding than  $e_g$  orbital. Six coordinated  $\text{Mn}^{3+}$  complexes show elongation along Z-axis.

20.Sol.  $p^4$  and  $d^3$  (Isolated state) are unsymmetrically filled. So, both are in electronically degenerate state.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (15)

- The observation of equal Cu – O distances in the hexa-coordinated Cu(II) complex  $K_2Pb[Cu(NO_2)_6]$  is best understood in terms of:
  - Failure of the Jahn-Teller theorem to predict the structure of this complex
  - Error in the crystallographic estimate of Cu – O distances
  - Dynamic Jahn-Teller distortion of Cu – O bonds
  - Symmetrical distribution of the nine valence electrons of Cu(II)
- Which of the following statements is true on the basis of complex  $[TiCl_6]^{3+}$  and  $[Ti(H_2O)_6]^{3+}$ 
  - $Z_{out}$  distortions are observed in both complexes
  - All bond lengths are equal in case of  $[TiCl_6]^{3-}$
  - $Z_{in}$  distortions are observed in case of  $[TiCl_6]^{3-}$
  - All of these
- Which of the following is false for distortion in  $[Cu(H_2O)_6]^{2+}$  —
  - Overall compound appears axially elongated.
  - Only ED state of orbitals undergo splitting
  - $Z_{out}$  dominates
  - $Z_{in}$  and  $Z_{out}$  both are present
- Which of the following statement is correct for complex  $[Cu(H_2O)_6]^{2+}$ .

(a) Only $Z_{out}$ exist	(b) $Z_{out}$ and $Z_{in}$ both exist
(c) only $Z_{in}$ exist	(d) All bond length are equal.
- Which of the following statements is true for solid  $MnF_3$  complex.
  - It has trigonal planar geometry.
  - It is perfect octahedral.
  - It is axially elongated.
  - It show triaxial distortion with Mn – F distance of 179, 191 and 209 pm (two each).

6. Which of the following is most distorted in their octahedral complex.  
 (a)  $\text{Cu}^{2+}$  (b)  $\text{Ag}^{2+}$  (c)  $\text{Au}^{2+}$  (d)  $\text{Mn}^{2+}$
7. Consider  $\text{MX}_6^{4-}$ ,  $\text{MY}_6^{4-}$ ,  $\text{MZ}_6^{4-}$  where  $\text{X} = \text{Cl}^-$ ,  $\text{Y} = \text{F}^-$ ,  $\text{Z} = \text{CN}^-$ . On the Basis of above information what is the correct order of Jahn Teller distortion in these complex.  
 (a)  $\text{MZ}_6^{4-} > \text{MY}_6^{4-} > \text{MX}_6^{4-}$  (b)  $\text{MX}_6^{4-} > \text{MY}_6^{4-} > \text{MX}_6^{4-}$   
 (c)  $\text{MY}_6^{4-} > \text{MX}_6^{4-} > \text{MZ}_6^{4-}$  (d)  $\text{MY}_6^{4-} > \text{MZ}_6^{4-} > \text{MX}_6^{4-}$
- 
8. Which of the following is static at room temperature  
 (a)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (b)  $\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  (c)  $\text{Ti}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  (d) All of these
9. What can you say about bond length of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  at  $100^\circ\text{C}$   
 (a) 2 longer and 4 shorter (b) 4 longer and 2 shorter  
 (c) all bond length are equal (d) three type of bond length are observed.
10. Which of the following statement are true.  
 (a)  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  remain dynamic at all range of temperature.  
 (b)  $\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  remain dynamic at all range of temperature.  
 (c)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is static at room temperature and axial bond are elongated.  
 (d)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and solid  $\text{CuF}_2$  remain static at all range of temperature.
11. Which of the following will not show dynamic JTD.  
 (a)  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  (b)  $\text{CrF}_2$  (c)  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  (d)  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$
12. In d-d- absorption band of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , band is split due to  
 (a) presence of octahedral geometry (b) Static Jahn-Teller distortion  
 (c) Dynamic Jahn-Teller distortion (d) Presence of trigonal bipyramidal geometry
13. For the given complexes (A), (B), (C) & (D) the ideal octahedral geometry will not be observed in  
 (A)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  (B)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  (C)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (D)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$   
 (a) (A) and (D) (b) (C) and (D) (c) (B) only (d) (D) only
14. Which of the following statement are true for  $\text{MnF}_3$ .  
 (a)  $Z_{\text{out}}$  distortions are observed as expected. (b) 4 long - 2 short bonds are observed.  
 (c)  $\text{Mn}-\text{F}$  bond distance are 179, 191 and 209 pm (two each)  
 (d) Triaxial distortions are observed.
15. Which of the following statements are true for  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$   
 (a) It is axially compressed. (b) All bond length are equal



- (c) It show dynamic Jahn Teller distortion (d) All of these
16. Which of the following complexes all bond length are equal due to feeble distortion.
- (a)  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  (b)  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$   
 (c)  $\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  (d) All of these
17. In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  all bond length are observed to be equal. The reason is—
- (a)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  does not show JTD  
 (b) Dynamic JTD in  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  but not in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (c) Dynamic JTD in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  but not in  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$   
 (d) Dynamic JTD is not observed in both
18. Which of the following statements is/are true for  $\text{CuF}_2$  and  $\text{KCuAlF}_6$ .
- (a) Axial bond are larger in both  $\text{CuF}_2$  and  $\text{KCuAlF}_6$ .  
 (b)  $\text{CuF}_2$  is axially elongated but  $\text{KCuAlF}_6$  is axially compressed.  
 (c)  $Z_{\text{out}}$  distortion are observed in  $\text{KCuAlF}_6$ .  
 (d)  $Z_{\text{in}}$  distortions are observed in  $\text{KCuAlF}_6$ .
19. How many from the following will show distortion in all range of temperature.  
 $\text{CrF}_2$ ,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{CuF}_2$ ,  $\text{CuCl}_2$ ,  $\text{MnCl}_3$

## ANSWER KEY

- |     |       |     |       |     |       |     |       |     |     |     |     |     |       |
|-----|-------|-----|-------|-----|-------|-----|-------|-----|-----|-----|-----|-----|-------|
| 1.  | (c)   | 2.  | (c)   | 3.  | (b)   | 4.  | (b)   | 5.  | (d) | 6.  | (c) | 7.  | (a)   |
| 8.  | (a)   | 9.  | (c)   | 10. | (c)   | 11. | (b)   | 12. | (a) | 13. | (d) | 14. | (c,d) |
| 15. | (b,c) | 16. | (a,b) | 17. | (a,c) | 18. | (b,d) | 19. | (4) |     |     |     |       |

## HINTS & SOLUTION

- 1Sol. Due to dynamic Jahn-Teller distortion all Cu – O bond length are observed to be equal.
- 2Sol. As configuration of  $Ti^{3+}$  in both complexes is  $d^1$ . Both are expected to be  $Z_{in}$ . But crystallographic study reveals that  $[TiCl_6]^{3-}$  show  $Z_{in}$  distortion and  $[Ti(H_2O)_6]^{3+}$  dynamic Jahn-Teller distortions are observed.
- 3.Sol. In case of  $[Cu(H_2O)_6]^{2+}$  both  $Z_{in}$  and  $Z_{out}$  distortion are present but  $Z_{out}$  dominates. It is not ED state which undergo splitting due to JTD but also Non ED state also split.
- 4.Sol. In case of  $[Cu(H_2O)_6]^{2+}$  both  $Z_{in}$  and  $Z_{out}$  distortion are present but  $Z_{out}$  dominates.
- 5.Sol. This complex  $MnF_3$  is triaxially elongated
- 6.Sol. As we move from  $3d \rightarrow 4d \rightarrow 5d$  distortion increases and  $Au^{2+}$  (octahedral) is most distorted.
- 7.Sol. According to spectrochemical series the strength of ligand varies as:  
 $CN^- > F^- > Cl^-$   
 As crystal field splitting increases Jahn Teller splitting also increases.
- 8.Sol. FOT of  $K_2Pb[Cu(NO_2)_6]$  and  $Tl_2Pb[Cu(NO_2)_6]$  are less than room temperature. Therefore at room temperature these will be dynamic.  
 But  $[Cu(H_2O)_6]^{2+}$  will show static JTD at room temperature.
- 9.Sol. At  $100^\circ C$   $[Cu(H_2O)_6]^{2+}$  is dynamic and all bond length are equal.
- 10.Sol.  $[Fe(H_2O)_6]^{2+}$  is dynamic due to feeble repulsion therefore remain dynamic at all range of temperature.  
 —  $K_2Pb[Cu(NO_2)_6]$  is dynamic due to berry pseudo rotation it become static at its FOT.  
 —  $[Cu(H_2O)_6]^{2+}$  is static at room temperature but can become dynamic if we increase temperature. But solid  $CuF_2$  is lattice in case of lattice berry pseudo rotation is not possible. Therefore it will remain static at all range of temperature.
11. Sol. As  $[Ti(H_2O)_6]^{3+}$ ,  $[Cu(H_2O)_6]^{2+}$ ,  $[Fe(H_2O)_6]^{2+}$  all are present in non-crystalline form and therefore can show dynamic JTD.  $CrF_2$  is a crystalline solid and berry pseudo rotation is not possible. Therefore it can not show dynamic JTD.
- 12Sol. Dynamic Jahn-Teller distortion is responsible for the band observed for  $[Fe(H_2O)_6]^{2+}$  complex.

**13Sol.** Due to Jahn-Teller distortion

Correct answer is (d)

14.Sol.  $Z_{out}$  distortions were expected but crystallographic study reveals triaxial distortion in complex  $MnF_6$ . Therefore three different bond length are expected in x, y and z direction.

15.Sol. In case of  $[Ti(H_2O)_6]^{3+}$  all bond lengths are equal due to dynamic Jahn Teller distortion.

16.Sol. In case of  $Ti(H_2O)_6^{3+}$  and  $Fe(H_2O)_6^{2+}$  weak or feeble distortion are found due to which all bond length appears to be equal as  $t_{2g}$  is unsymmetrically filled

17.Sol. In case of  $[Ni(H_2O)_6]^{2+}$  all bond length are equal to as no JTD is observed in this complex. But in case of  $[Fe(H_2O)_6]^{2+}$  all bond length are equal to due to dynamic JTD.

18.Sol.  $CuF_2$  is axially elongated as  $e_g$  is unsymmetrically filled. But in case of  $KCuAlF_6$  due to lattice packing equatorial bonds are large as these are present at bridging. Therefore over all complex is found to be axially compressed.

Sol. In case of  $CrF_2$ ,  $CuF_2$ ,  $CuCl_2$ ,  $MnCl_3$  JTD is static and at remain static it all range of temperature therefore always distorted. But in case of  $[Cu(H_2O)_6]^{2+}$ , it is static at room temperature but becomes dynamic as we increase the temperature.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (16)

- Number of microstates in term  $^1G$  is  
(a) 9 (b) 6 (c) 7 (d) 15
- The ground state term symbol for high spin  $d^5s^1$  configuration is  
(a)  $^3S$  (b)  $^6P$  (c)  $^7S$  (d)  $^7P$
- What terms can arise from the configuration  $2p^13p^1$ ?  
(a)  $^3D, ^1D, ^3P, ^1P, ^3S, ^1S$  (b)  $^3D, ^3P, ^3S$   
(c)  $^1D, ^1P, ^1S$  (d)  $^3D, ^1P, ^3S$
- The lowest energy state of Be having configuration  $1s^2 2s^1 3s^1$  is  
(a)  $^1S_0$  (b)  $^1D_2$  (c)  $^3S_1$  (d)  $^3P_1$
- The ground state term symbol for the excited state of Helium is  
(a)  $^3S_0$  (b)  $^3S_1$  (c)  $^1S_0$  (d)  $^1S_1$
- For  $p^2$  configuration, second excited state term is  
(a)  $^1D$  (b)  $^3P$  (c)  $^3F$  (d)  $^1S$
- Term symbol for Boron is  
(a)  $^3P_{3/2}$  (b)  $^3P_{1/2}$  (c)  $^3F_{1/2}$  (d)  $^3P_0$
- The term symbol for an atom with the configuration  $s^1p^1$  is:—  
(a)  $^1S$  (b)  $^3P$  (c)  $^3S$  (d)  $^1D$
- The ground state for  $p^6$  is same for  
(a)  $d^{10}$  (b)  $d^6$  (c)  $p^3$  (d)  $d^5$
- The ground state for  $2p^3$  is  
(a)  $^4S_3$  (b)  $^3P_4$  (c)  $^4S_{3/2}$  (d)  $^2P_1$

11. What is the ground term of the configurations  $3d^5$  of  $Mn^{2+}$  and  $3d^3$  of  $Cr^{3+}$  respectively  
 (a)  $^6S$  &  $^4F$  (b)  $^3S$  &  $^1P$  (c)  $^4S$  &  $^3P$  (d)  $^4S$  &  $^4P$
12. For  $d^2$  configuration, correct energy order of states is :-  
 (a)  $^3F > ^3P < ^1G < ^1D < ^1S$  (b)  $^3F < ^1D < ^3P < ^1G < ^1S$   
 (c)  $^1G > ^3F < ^1D < ^3P < ^1S$  (d)  $^3F = ^3P < ^1G = ^1D = ^1S$
13. What is ground state of  $Cr^{2+}$  specifying value of J is:  
 (a)  $^5D_4$  (b)  $^5D_0$  (c)  $^5D_1$  (d)  $^5D_3$
14. Ground state term for  $d^7$  system is  
 (a)  $^4F$  (b)  $^4F_{9/2}$  (c)  $^3F$  (d)  $^3F_2$
15. Ground state term for  $d^2$  configuration is  
 (a)  $^3F$  (b)  $^3P$  (c)  $^1G$  (d)  $^1S$
16. Mulliken symbol for spectroscopic term P in octahedral field is:  
 (a)  $A_{1g}$  (b)  $T_{1g}$  (c)  $T_{2g}$  (d)  $E_g$
17. Possible terms for Si having configuration  $3s^23p^2$  are  $^1D_2$ ,  $^3P_2$ ,  $^3P_1$ ,  $^3P_0$  and  $^1S_0$  which of the following is ground state term for Si.  
 (a)  $^1D_2$  (b)  $^1S_0$  (c)  $^3P_0$  (d)  $^3P_2$
18. What is ground state term for  $Gd^{3+}$   
 (a)  $^8S$  (b)  $^8D$  (c)  $^5S$  (d) None
19. Which of the following terms are possible for Nitrogen having configuration  $2s^22p^3$   
 (a)  $^4S$  (b)  $^2D$  (c)  $^4D$  (d)  $^2P$
20. How many microstate are possible for  $d^2$  configuration, including both weak and strong field ligands?

### ANSWER KEY

- |         |         |         |         |             |          |         |
|---------|---------|---------|---------|-------------|----------|---------|
| 1. (a)  | 2. (c)  | 3. (a)  | 4. (c)  | 5. (b)      | 6. (d)   | 7. (b)  |
| 8. (b)  | 9. (a)  | 10. (c) | 11. (a) | 12. (b)     | 13. (b)  | 14. (a) |
| 15. (a) | 16. (b) | 17. (c) | 18. (a) | 19. (a,b,c) | 20. (45) |         |

## HINTS & SOLUTION

**1.Sol.** Number of microstates in term  $^1G$  is

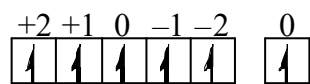
$$(2S + 1)(2L + 1)$$

$$(2 \times 0 + 1)(2 \times 4 + 1)$$

$$= 9$$

Correct option is (a)

**2.Sol.**  $d^5 s^1$



$$L = 0 \qquad S = 3$$

$$2S + 1 = 7$$

term  $^7S$

Correct option is (c)

**3.Sol.** Term that can arise for  $2p^1 3p^1$  configuration.

$$l_1 = 1 \qquad l_2 = 1$$

$$L = |l_1 + l_2| \dots \dots \dots |l_1 - l_2|$$

$$= |1 + 1| \dots \dots \dots |1 - 1|$$

$$= 2, 1, 0$$

$$s_1 = \frac{1}{2} \qquad s_2 = \frac{1}{2} \qquad S = |s_1 + s_2| \dots \dots |s_1 - s_2|$$

$$= \left| \frac{1}{2} + \frac{1}{2} \right| \dots \dots \left| \frac{1}{2} - \frac{1}{2} \right|$$

$$= 1, 0$$

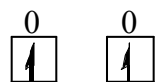
$$2S + 1 = 2 \times 1 + 1 = 3$$

$$2S + 1 = 2 \times 0 + 1 = 1$$

term that can arise are  $^3D$ ,  $^1D$ ,  $^3P$ ,  $^1P$ ,  $^3S$ ,  $^1S$

Correct option is (a)

**4.Sol.** Be @  $2s^1 3s^1$



$$L = 0 \qquad S = 1$$

$$2S + 1 = 3$$

$$J = |L + S| = |0 + 1|$$

$$J = 1$$

$$^3S_1$$

Correct option is (c)

5.Sol. Excited state of Helium is  $\begin{array}{|c|} \hline 0 \\ \hline \uparrow \\ \hline 1S \end{array}$   $\begin{array}{|c|} \hline 0 \\ \hline \uparrow \\ \hline 2S \end{array}$

$$L = 0$$

$$S = 1$$

$$2S + 1 = 3$$

$$J = L + S = 1$$

term symbol for excited state is  $^3S_1$

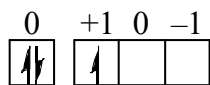
6.Sol. Possible terms for  $P^2$  configuration are  $3P$ ,  $^1D$ ,  $^1S$

$$^3P < ^1D < ^1S$$

Second excited state term is  $^1S$

Correct option is (d)

7.Sol. Electronic configuration of Boron is  $1s^2 2s^2 2p^1$



$$L = 1$$

$$S = 1/2$$

$$|L - S| = \left| 1 - \frac{1}{2} \right| = 1/2$$

Term symbol  $^3P_{1/2}$

Correct option is (b)

8.Sol.  $s^1 p^1 \rightarrow \begin{array}{|c|} \hline 0 \\ \hline \uparrow \\ \hline \end{array} \begin{array}{|c|} \hline +1 \\ \hline \uparrow \\ \hline \end{array} \begin{array}{|c|} \hline 0 \\ \hline \\ \hline \end{array} \begin{array}{|c|} \hline -1 \\ \hline \\ \hline \end{array}$

$$L = 1$$

$$S = 1$$

$$^3P$$

Correct option is (b)

9.Sol. As  $\begin{array}{|c|} \hline +1 \\ \hline \uparrow\downarrow \\ \hline \end{array} \begin{array}{|c|} \hline 0 \\ \hline \uparrow\downarrow \\ \hline \end{array} \begin{array}{|c|} \hline -1 \\ \hline \uparrow\downarrow \\ \hline \end{array} \begin{array}{|c|} \hline +2 \\ \hline \uparrow\downarrow \\ \hline \end{array} \begin{array}{|c|} \hline +1 \\ \hline \uparrow\downarrow \\ \hline \end{array} \begin{array}{|c|} \hline 0 \\ \hline \uparrow\downarrow \\ \hline \end{array} \begin{array}{|c|} \hline -1 \\ \hline \uparrow\downarrow \\ \hline \end{array} \begin{array}{|c|} \hline -2 \\ \hline \uparrow\downarrow \\ \hline \end{array}$

$$S = 0$$

$$S = 0$$

$$L = 0$$

$$L = 0$$

$$^1S$$

$$^1S$$

For fully filled configuration ground state is  $^1S$

Correct option is (a)

10.Sol.  $\begin{array}{|c|} \hline +1 \\ \hline \uparrow \\ \hline \end{array} \begin{array}{|c|} \hline 0 \\ \hline \uparrow \\ \hline \end{array} \begin{array}{|c|} \hline -1 \\ \hline \uparrow \\ \hline \end{array}$

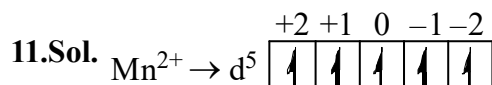
$$L = 0$$

$$S = 3/2$$

$$J = L + S$$

$$= 0 + 3/2$$

Term symbol  ${}^4S_{3/2}$



$$L = 0$$

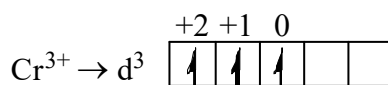
$$S = 5/2$$

$$2S + 1 = 2 \times \frac{5}{2} + 1$$

$$= 6$$

$${}^6S$$

Correct option is (a)



$$L = 3$$

$$S = 3/2$$

$$2S + 1 = 2 \times \frac{3}{2} + 1$$

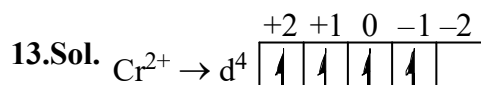
$$= 4$$

$${}^4F$$

12.Sol. To arrange the term in order of energy first we compare S value the term having higher S value is lower in energy. Then we compare L value. The term having highest L value is lower in energy.

In case of  $d^2$  configuration order of energy also depends upon Racah Parameter

Correct order of energy of term is



$$L = 2$$

$$S = 2$$

$$J = |L + S| = 4 \quad |L - S| = |2 - 2| = 0$$

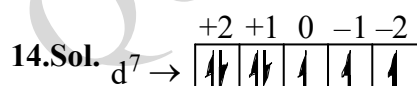
For less than half filled take minimum J value.

Therefore, term symbol for  $Cr^{2+}$  is  ${}^5D_0$

Correct option is (b)

$${}^3F < {}^1D < {}^3P < {}^1G < {}^1S$$

Correct option is (b)



$$L = 3$$

$$S = 3/2$$

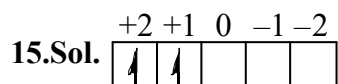
$$= 2S + 1 = 2 \times \frac{3}{2} + 1 = 4$$

$$J = |L + S| = \left| 3 + \frac{3}{2} \right| = \frac{9}{2}$$

Ground state term is  ${}^4F$  and term symbol is  ${}^4F_{9/2}$

Correct option is (a)





$$L = 3$$

$$S = 1$$

Ground state term is  ${}^3F$

16.Sol. Mulliken symbol for spectroscopic term P is  $T_{1g}$

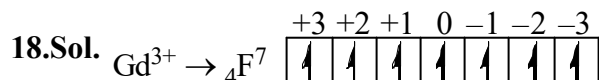
Correct option is (b)

7.Sol. First we compare S value then L value

$$\text{Energy} \propto S \text{ value} \propto \frac{1}{L \text{ value}}$$

Therefore ground state term is  ${}^3P_0$

Correct option is (c)



$$L = 0$$

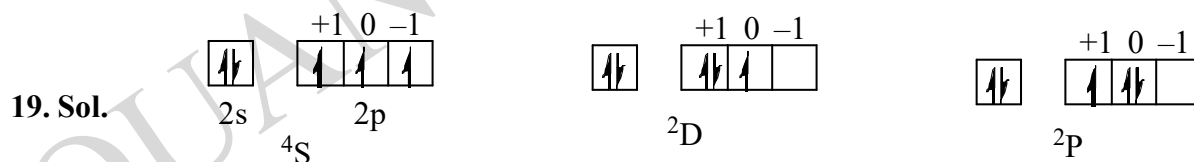
$$S = 7/2$$

$$2S+1 = 2 \times \frac{7}{2} + 1$$

$$= 8$$

term  ${}^8S$

Correct option is (a)



So, possible term for Nitrogen are  ${}^4S$ ,  ${}^2P$ ,  ${}^2D$ .

Correct option is a, b, d

20. Sol. No. of microstate  $= \frac{10!}{2!8!} = \frac{10 \times 9 \times 8!}{2 \times 8!} = 45$

Correct answer is 45



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (17)

- If the metal is in high oxidation state and ligands contain non bonding electrons then
  - Metal to ligand charge transfer transition are observed
  - Ligand to ligand charge transfer transition are observed
  - Ligand to metal charge-transfer transition are observed
  - Intra ligand charge transfer transition are observed.
- What is the correct order of  $\lambda_{\text{LMCT}}$  for the following complexes.
  - $\text{VO}_4^{3-} < \text{CrO}_4^{2-} < \text{MnO}_4^-$
  - $\text{VO}_4^{3-} < \text{MnO}_4^- < \text{CrO}_4^{2-}$
  - $\text{MnO}_4^- < \text{CrO}_4^{2-} < \text{VO}_4^{3-}$
  - $\text{CrO}_4^{2-} < \text{MnO}_4^- < \text{VO}_4^{3-}$
- The electron transfer in LMCT is laporte \_\_\_\_\_ and spin \_\_\_\_\_.
  - allowed, allowed
  - allowed, forbidden respectively
  - forbidden, allowed respectively
  - forbidden, forbidden
- Cu(II) forms a faint pink coloured complex with o-phenanthroline. When this complex is reduced, the colour of this compound disappears. The colour of compound is due to
  - MLCT
  - LMCT
  - d-d transition
  - Intra Valence Charge Transfer
- The colour of  $\text{trans}[\text{Co}(\text{en})_2\text{F}_2]^+$  is less intense than that of  $\text{cis}[\text{Co}(\text{en})_2\text{F}_2]^+$ . This is due to
  - cis isomer is more stable
  - trans isomer is more stable
  - due to Jahn-Teller distortion
  - due to decrease in symmetry from trans to cis.
- The pertechnetate ion,  $\text{TcO}_4^-$  is often used to introduce the radioactive Tc into compounds, some of which are used as medical tracers. Unlike the isoelectronic, vividly purple permanganate ion, pertechnetate is very pale red.

The colour of pertechnetate ion is due to

- (a) LMCT (b) MLCT  
(c) d-d transition (d) Intra Valence Charge Transfer

7.  $\text{MnO}_4^-$  is deep purple but  $\text{TcO}_4^-$  is pale red this is due to

- (a) d-d transition are responsible which are laporte forbidden  
(b) the separation between donor orbital and acceptor orbital is lesser in  $\text{MnO}_4^-$   
(c) the separation between donor orbital and acceptor orbital is lesser in  $\text{TcO}_4^-$   
(d) In  $\text{TcO}_4^-$  transitions are spin forbidden

8. For which of the following ions, the colour is NOT due to a d-d transition?

- (a)  $\text{CrO}_4^{2-}$  (b)  $\text{Cu}(\text{NH}_3)_4^{2+}$  (c)  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  (d)  $\text{CoF}_6^{3-}$

9. The intense colour of  $\text{KFe}[\text{Cr}(\text{CN})_6]$  is due to

- (a) MLCT (b) LMCT (c) d-d transition  
(d) Intra Valence Charge Transfer

10. The intense blue colour  $[\text{Re}_2\text{Cl}_8]^{2-}$  is due to

- (a)  $\pi-\pi^*$  transition (b)  $n-\pi^*$  transition (c)  $\delta-\delta^*$  transition (d)  $n-\alpha^*$  transition

11. The compound which shows  $\text{L} \leftarrow \text{M}$  charge transfer is:

- (a)  $\text{Ni}(\text{CO})_4$  (b)  $\text{K}_2\text{Cr}_2\text{O}_7$  (c)  $\text{HgO}$  (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

12. In the isoelectronic series,  $\text{VO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$  and  $\text{MnO}_4^-$  all members have intense charge transfer (CT) transitions. The incorrect statement is

- (a) CT transitions are attributed to excitations of electrons from ligand ( $\sigma$ ) to metal (e)  
(b)  $\text{MnO}_4^-$  exhibits charge transfer at shortest wavelength among the three  
(c) The wavelengths of transitions increase in the order  $\text{VO}_4^{3-} < \text{CrO}_4^{2-} < \text{MnO}_4^-$   
(d) The charge on metal nucleus increases in the order  $\text{VO}_4^{3-} < \text{CrO}_4^{2-} < \text{MnO}_4^-$

13. The intense red color of  $[\text{Fe}(\text{bpy})_3]^{2+}$  (bpy = 2, 2' -bipyridine) is due to

- (a) metal-to-ligand charge transfer (MLCT) (b) ligand-to-metal charge transfer (LMCT)  
(c) d-d transition (d) inter-valence charge transfer (IVCT)

14. The oxidizing power of  $[\text{CrO}_4]^{2-}$ ,  $[\text{MnO}_4]^{2-}$  and  $[\text{FeO}_4]^{2-}$  follows the order

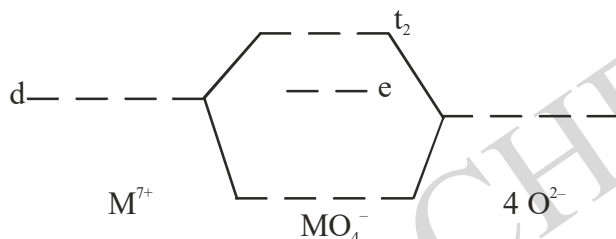
- (a)  $[\text{CrO}_4]^{2-} < [\text{MnO}_4]^{2-} < [\text{FeO}_4]^{2-}$  (b)  $[\text{FeO}_4]^{2-} < [\text{MnO}_4]^{2-} < [\text{CrO}_4]^{2-}$   
 (c)  $[\text{MnO}_4]^{2-} < [\text{FeO}_4]^{2-} < [\text{CrO}_4]^{2-}$  (d)  $[\text{CrO}_4]^{2-} < [\text{FeO}_4]^{2-} < [\text{MnO}_4]^{2-}$
15. The complex  $[\text{FeCl}_4]^{2-}$  is colourless due to  
 (a) d-d transition (b) d-d transitions are spin forbidden  
 (c) absorb in IR region (d) None of these
16. Which of the following statements are true?  
 (a) Ligand to metal charge transfer (LMCT) are laporte allowed as well as spin allowed.  
 (b) LMCT energy is directly proportional to oxidation state  
 (c)  $\lambda_{\text{LMCT}}$  increases with increase in oxidation state  
 (d) Generally intensity of transition is inversely proportional to LMCT energy.
17. Which of the following are correct order of wavelength.  
 (a)  $\text{MnO}_4^- > \text{TcO}_4^- > \text{ReO}_4^-$  (b)  $\text{FeCl}_4^{2-} > \text{FeBr}_4^{2-}$   
 (c)  $\text{CrO}_4^{2-} > \text{MoO}_4^{2-} > \text{WO}_4^{2-}$  (d)  $\text{OsCl}_6^{3-} > \text{OsCl}_6^{2-}$
18. Which of the following statements are correct.  
 (a) Electronic transition for high spin  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  is spin forbidden, but for  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is spin allowed.  
 (b) Aqueous solutions of  $[\text{MnO}_4]^-$  are purple whereas those of  $[\text{ReO}_4]^-$  are colourless  
 (c) The colour of trans  $[\text{Co}(\text{en})_2\text{F}_2]^+$  is more intense than trans  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (d) All of these
19. Laporte-forbidden, spin allowed transitions are observed in how many complexes.  
 $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{MnO}_4^{2-}$

## ANSWER KEY

- |     |     |     |           |     |        |     |        |     |     |     |     |     |     |
|-----|-----|-----|-----------|-----|--------|-----|--------|-----|-----|-----|-----|-----|-----|
| 1.  | (c) | 2.  | (a)       | 3.  | (a)    | 4.  | (c)    | 5.  | (d) | 6.  | (a) | 7.  | (b) |
| 8.  | (a) | 9.  | (d)       | 10. | (c)    | 11. | (a)    | 12. | (b) | 13. | (a) | 14. | (a) |
| 15. | (c) | 16. | (a, c, d) | 17. | (a, c) | 18. | (a, b) | 19. | (2) |     |     |     |     |

## HINTS & SOLUTION

- 1.Sol. When metal is present in high oxidation state and  $\pi$ -donor ligand are present then ligand to metal charge transfer take place.
- 2.Sol. As in all the three complexes only LMCT is observed. Therefore as the oxidation state increases  $\lambda_{\text{LMCT}}$  increases.
- 3.Sol. In LMCT transition take place from p-orbital to ligand to d-orbital or s-orbital or metal. Therefore LMCT is laporte as well as spin allowed.
- 4.Sol. Cu(II) has  $d^9$  configuration and d-d transition can take place which is responsible for the colour of complex as it is reduced the configuration change to  $d^{10}$ . Now d-d transition are not possible. Therefore colour disappear.
- 5.Sol. As the molecule or complex becomes more unsymmetrical laporte selection rule is relaxed and more intense colour is observed for  $\text{cis}[\text{Co}(\text{en})_2\text{F}_2]^+$
- 6.Sol. These colours are most likely the consequence of LMCT transitions, from orbitals that are primarily from the oxides ligands to orbitals that are primarily from the metal.

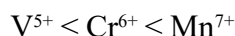


- 7.Sol. In  $\text{TcO}_4^-$ , the separation between the donor orbitals of the  $\text{O}^{2-}$  ligands and the acceptor orbitals is greater than in  $\text{MnO}_4^-$ . As a consequence,  $\text{TcO}_4^-$  absorb light of high energy than  $\text{MnO}_4^-$ . Most of the absorption in case of  $\text{TcO}_4^-$  is in the ultraviolet, with the pale red colour a result of a tail of absorption band extending into visible.
- 8.Sol. The colour of  $\text{CrO}_4^{2-}$  is due to charge transfer not due to d-d- transition.
- 9.Sol. Here intravalence charge transfer take place between  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  redox pair which is responsible for colour.
- 10.Sol. The intense blue colour of  $[\text{Re}_2\text{Cl}_8]^{2-}$  is due to  $\delta-\delta^*$  transition as this energy gap lies in the visible region.
- 11.Sol. The compound  $\text{Ni}(\text{CO})_4$  will show metal to ligand charge transfer as metal has high electron density and ligand is  $\pi$ -acceptor.

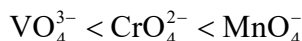
- 12.Sol. CT (charge transfer) transitions are attributed to excitations of electron from ligand to metal or vice-versa.

Higher the oxidizing state of metal, higher is the wavelength of transition.

Order of oxidizing state is



$\therefore$  The order of wavelength of transition is



$\text{MnO}_4^-$  have high oxidation state.

So, energy gap will be less and wavelength will be maximum.

Correct option is (b)

- 13.Sol. Electronic configuration of  $\text{Fe}^{2+} = [\text{Ar}] 3d^6$  and bpy (2, 2'-bipyridine) is an aromatic ligand with low lying  $\pi^*$  orbital, so metal ( $\text{Fe}^{2+}$ ) transfers its electron to  $\pi^*$  system of the ligand due to which, its colour is intense red. (MLCT).

Correct option is (a)

**14.Sol.**  $\text{CrO}_4^{2-} < \text{MnO}_4^{2-} < \text{FeO}_4^{2-}$

All have +6 oxidation state but due to smaller size on going from Cr to Fe. Fe has very high charge density. Hence, it has very high tendency to accept electron. Hence, strongest oxidising agent.

**Correct option is (a)**

**15.Sol.** The complex  $[\text{FeCl}_4]^{2-}$  is colourless because it absorb in IR region. The complex will impart colour if it absorb in visible region.

**6.Sol.** LMCT transition are both LA as well as spin allowed.

$$\text{LMCT Energy} \propto \frac{1}{\text{Oxidation state}}$$

$$\lambda_{\text{MLCT}} \propto \text{oxidation state}$$

$$\text{Intensity} \propto \frac{1}{\text{LMCT energy}}$$

As high LMCT energy transition falls UV region.

**17.Sol.** As we move from 3d  $\rightarrow$  4d  $\rightarrow$  5d LMCT energy gap increases and wavelength decreases.

As Cl is stronger ligand as compared to Br so,  $[\text{FeBr}_4]^{2-}$  will have greater wavelength.

As oxidation state of metal increases LMCT energy decreases and wavelength increases.

**18.Sol.** Complex of  $d^5$  (HS) show spin forbidden transition but  $d^7$  (HS) complex show spin allowed transition.

As we move from 3d  $\rightarrow$  4d  $\rightarrow$  5d LMCT energy gap increases and for  $\text{ReO}_4^-$  it lies in UV region and therefore colourless.

The colour of trans  $[\text{Co}(\text{en})_2\text{F}_2]^+$  is less intense as compared to trans  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  as energy gap in more is case of trans  $[\text{Co}(\text{en})_2\text{F}_2]^+$  therefore intensity will be less.

$$\text{Intensity} \propto \frac{1}{\text{energy}}$$

**19.Sol.** Transition in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  are spin allowed but laporte forbidden. Transition in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  are both spin forbidden as well as laporte forbidden

Transitions in  $[\text{MnO}_4]^{2-}$  are spin allowed as well as laporte allowed.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (19)

- The asymmetric nature of visible absorption bond of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is due to  
(a) Laporte's allowed transition (b) Laporte's forbidden transition  
(c) Dynamic Jahn-Teller (d) Intensity stealing transition
- In the absorption spectra of  $[\text{TiCl}_6]^{3-}$  the two peaks are separated approximately by  
(a)  $700 \text{ cm}^{-1}$  (b)  $1100 \text{ cm}^{-1}$  (c)  $1400 \text{ cm}^{-1}$  (d)  $1900 \text{ cm}^{-1}$
- What is the ground state term for  $\text{Ti}^{3+}$  in  $[\text{TiCl}_6]^{3-}$  complex.  
(a)  ${}^2A_{1g}$  (b)  ${}^2B_{1g}$  (c)  ${}^2B_{2g}$  (d)  ${}^2T_{2g}$
- In complex ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  absorption maximum and shouldering is observed at:  
(a)  $25700 \text{ cm}^{-1}$ ,  $18000 \text{ cm}^{-1}$  respectively (b)  $20300 \text{ cm}^{-1}$ ,  $17400 \text{ cm}^{-1}$  respectively  
(c)  $20300 \text{ cm}^{-1}$ ,  $18000 \text{ cm}^{-1}$  respectively (d)  $23700 \text{ cm}^{-1}$ ,  $17400 \text{ cm}^{-1}$  respectively
- For  $[\text{CoF}_6]^{3-}$  absorption occur from  
(a)  ${}^5E_g \rightarrow {}^5T_{2g}$  (b)  ${}^5T_{2g} \rightarrow {}^5E_g$  (c)  ${}^1E_g \rightarrow {}^1T_{2g}$  (d)  ${}^1T_{2g} \rightarrow {}^1E_g$
- The absorption peak responsible for the blue colour of  $[\text{CoF}_6]^{3-}$  is observed at  
(a)  $15000 \text{ cm}^{-1}$  (b)  $13100 \text{ cm}^{-1}$  (c)  $27500 \text{ cm}^{-1}$  (d)  $11000 \text{ cm}^{-1}$
- How many absorption peak are observed in electronic spectra of  $[\text{CoF}_6]^{3-}$   
(a) 2 (b) 1 (c) 3 (d) 4
- The absorption band in electronic spectra of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is usually found in between  
(a)  $1500 - 17000 \text{ cm}^{-1}$  (b)  $10,000 - 11000 \text{ cm}^{-1}$   
(c)  $12000 - 13000 \text{ cm}^{-1}$  (d)  $25,000 - 27,000 \text{ cm}^{-1}$
- Which transition is forbidden in electronic spectra of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$   
(a)  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  (b)  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  (c)  ${}^2B_{1g} \rightarrow {}^2E_g$  (d) None of the above
- The blue colour  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complex absorbs in the visible region at  
(a)  $15000 \text{ cm}^{-1}$  (b)  $7500 \text{ cm}^{-1}$  (c)  $12000 \text{ cm}^{-1}$  (d)  $21000 \text{ cm}^{-1}$
- The more intense peak is observed in the electronic spectra of  $d^1(\text{Td})$  in comparison to  $d^1(\text{Oh})$  this is due to  
(a) charge transfer (b) d-d transition (c) p-d mixing (d) None of these
- The transition observed in electronic spectra of  $[\text{CuCl}_4]^{2-}$  is due to  
(a)  ${}^2E \rightarrow {}^2T_2$  (b)  ${}^2T_2 \rightarrow {}^2E$  (c)  ${}^2B_{1g} \rightarrow {}^2T_{1g}$  (d)  ${}^2E \rightarrow {}^2A_1$

13. While drawing correlation diagram for  $d^2$  system the terms 'G', 'D' and 'S' are not included because
- These terms are higher in energy
  - These terms are lower in energy
  - The spin multiplicity does not match with ground state term.
  - The spin multiplicity does not match with excited state term.
14. In  $d^2$  system when the ground state term  $^3F$  split into three state, the spin multiplicity will
- increases
  - decrease
  - may increase or decrease
  - will remain same
15. Calculate CFSE of a complex  $[\text{TiL}_6]^{2+}$  given that the transition in its electronic spectra are observed at  $109700 \text{ cm}^{-1}$ ,  $109900 \text{ cm}^{-1}$ ,  $110400 \text{ cm}^{-1}$
16. Three bands in the electronic spectrum of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  are due to following transitions
- (A)  $^4T_{2g} \rightarrow ^4T_{1g}$                       (B)  $^4A_{2g} \rightarrow ^4T_{2g}$                       (C)  $^4A_{2g} \rightarrow ^2E_g$
- Identify the correct statement about them
- Intensity of (A) is lowest
  - Intensity of (C) is lowest
  - Intensity of (A), (B) and (C) are similar
  - Intensity of (B) and (D) are similar
17. Ruby has a low concentration of a trivalent 3d-metal ion substituted for  $\text{Al}^{3+}$  in alumina giving initial excitations of the spin-allowed process  $^4T_{2g} \leftarrow ^4A_{2g}$  and  $^4T_{1g} \leftarrow ^4A_{2g}$ . The 3d-metal ion is:
- Cr(III)
  - Fe(III)
  - Co(III)
  - Ni(III)
18. Which one of the following octahedral complex shows  $^3T_{2g} \leftarrow ^3A_{2g}$  transition as the lowest energy visible band in its electronic spectrum?
- $[\text{Cr}(\text{NH}_3)_6]^{3+}$
  - $[\text{FeF}_6]^{3-}$
  - $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
19. Three electronic transitions at  $14900$ ,  $22700$  and  $34400 \text{ cm}^{-1}$  are observed in the absorption spectrum of  $[\text{CrF}_6]^{3-}$ . The  $\Delta_0$  value (in  $\text{cm}^{-1}$ ) and the corresponding transition are
- $7800$  and  $^4A_{2g} \rightarrow ^4T_{2g}$
  - $14900$  and  $^4A_{2g} \rightarrow ^4T_{2g}$
  - $14900$  and  $^4T_{2g} \rightarrow ^4T_{1g}$  (F)
  - $7800$  and  $^4T_{2g} \rightarrow ^4T_{1g}$  (F)
20. Which of the following statements is incorrect?
- The electronic spectrum of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  contain 3 absorptions
  - Absorption in the electronic spectrum of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  are extremely weak.
  - For a tetrahedral  $d^4$  complex, 3 absorptions are expected in its electronic spectrum.
  - The absorption in the electronic spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is assigned to the  $E_g \leftarrow T_{2g}$  transition.

## ANSWER KEY

- |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (c) | 2.  | (c) | 3.  | (c) | 4.  | (b) | 5.  | (a) | 6.  | (b) | 7.  | (b) |
| 8.  | (b) | 9.  | (a) | 10. | (c) | 11. | (c) | 12. | (b) | 13. | (c) | 14. | (d) |
| 15. | (a) | 16. | (b) | 17. | (a) | 18. | (d) | 19. | (b) | 20. | (c) |     |     |



## HINTS & SOLUTION

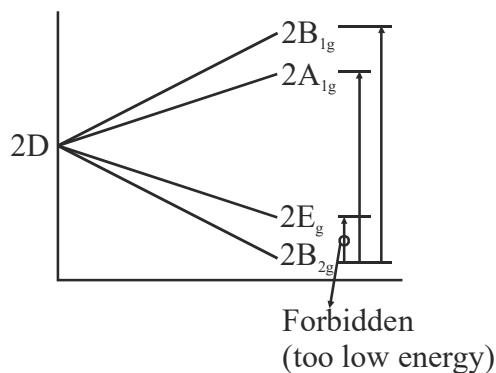
**1.Sol.** (c) The asymmetric nature observed in spectra of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is due to dynamic Jahn – Teller distortion. Due to dynamic JTD the  $T_{2g}$  and  $E_g$  level split further.

**2.Sol.** (c)  $1400\text{ cm}^{-1}$

The two absorption peaks observed in electronic spectra of  $[\text{TiCl}_6]^{3-}$  due to transition from  ${}^2B_{2g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{2g} \rightarrow {}^2B_{1g}$  are separated by  $1400\text{ cm}^{-1}$

**3.Sol.** (c)  ${}^2B_{2g}$

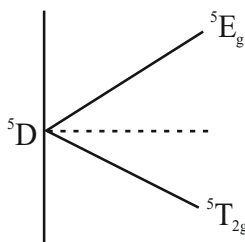
The ground state term for  $\text{Ti}^{3+}$  in  $[\text{TiCl}_6]^{3-}$  complex is  ${}^2B_{2g}$ .



**4.Sol.** (b)  $20300\text{ cm}^{-1}$ ,  $17400\text{ cm}^{-1}$  respectively

In the complex ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  absorption maximum observed at  $20300\text{ cm}^{-1}$  and also the absorption maximum has shoulder at  $17400\text{ cm}^{-1}$  because of dynamic JTD.

**5.Sol.** The ground state term of  $[\text{CoF}_6]^{3-}$  is  ${}^5D$ . In high spin octahedral complexes  ${}^5D$  term splits high spin octahedral complexes  ${}^5D$  term splits into  ${}^5T_{2g}$  and  ${}^5E_g$ . So, electronic transition from  ${}^5T_{2g} \rightarrow {}^5E_g$  is observed.

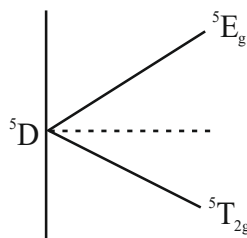


**6.Sol.** (b)  $13100\text{ cm}^{-1}$

The absorption peak responsible for blue colour of  $[\text{CoF}_6]^{3-}$  is observed at  $13100\text{ cm}^{-1}$

7.Sol. (b)

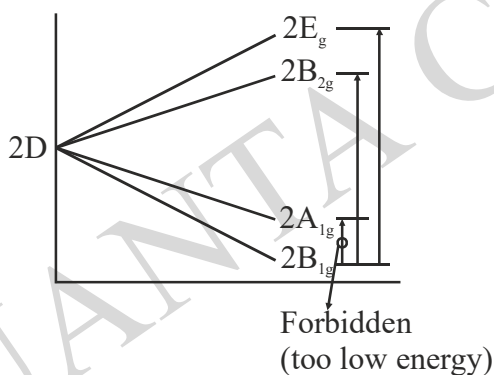
The ground state term of  $[\text{CoF}_6]^{3-}$  is  ${}^5\text{D}$ . In high spin octahedral complexes  ${}^5\text{D}$  term splits into  ${}^5\text{T}_{2g}$  and  ${}^5\text{E}_g$ . So, only one electronic transition is observed from  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ .

8.Sol. (b)  $10,000 - 11,000 \text{ cm}^{-1}$ 

The absorption band in electronic spectra of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is usually found in between  $10,000$  to  $11,000 \text{ cm}^{-1}$ .

9.Sol. (a)

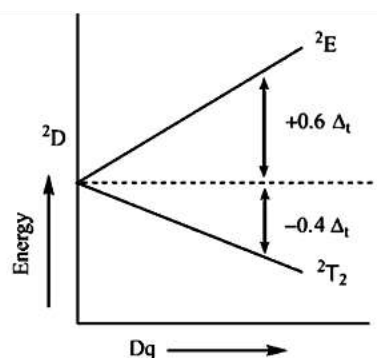
The transition from  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  is forbidden in  $\text{Cu}^{2+}$  ion spectra.

10.Sol. (c)  $12000 \text{ cm}^{-1}$ 

11.Sol. (c) p-d mixing

The intensity of peak observed in tetrahedral is more because in tetrahedral p-d mixing is observed and these transition becomes laporte allowed transition.

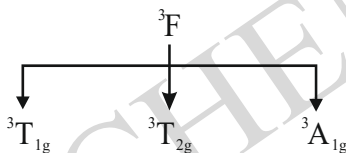
12.Sol. (b)  ${}^2\text{T}_2 \rightarrow {}^2\text{E}$



13.Sol. (c) In correlation diagram only those terms are included whose spin multiplicity match with ground state. The ground state term for  $d^2$  system is  ${}^3F$ . So, only those term which have multiplicity 3 are included.  ${}^3F$  and  ${}^3P$  are only observed in diagram.

14.Sol. (d) will remain same

During splitting of term the spin multiplicity do not split it remains same



15.Sol. In case of  $d^2$  system  $\Delta_0 = \bar{\nu}_3 - \bar{\nu}_1$

$$\Delta_0 = 110400 - 109700$$

$$= 700 \text{ cm}^{-1}$$

$$\text{CFSE} = -0.8 \Delta_0 \text{ (for } d^2\text{)}$$

$$= -0.8 \times 700$$

$$= -560 \text{ cm}^{-1}$$

$$\frac{-560}{83.5} \text{ kJ/mol} = -6.69 \text{ kJ/mol}^{-1}$$

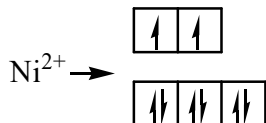
16.Sol. Intensity of  $C \left( {}^4A_{2g} \rightarrow {}^2E_g \right)$  is lowest, since it is spin forbidden.

**Correct answer is (b)**

17.Sol. (a)  $\text{Cr}^{3+}$

$\text{Cr}^{3+}$  metal ion is responsible for the red colour shown by Ruby which is due to red phosphorescence from  ${}^2E_g \rightarrow {}^1A_{2g}$ .

18.Sol. (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$



$$S = \frac{1}{2} + \frac{1}{2} = 1$$

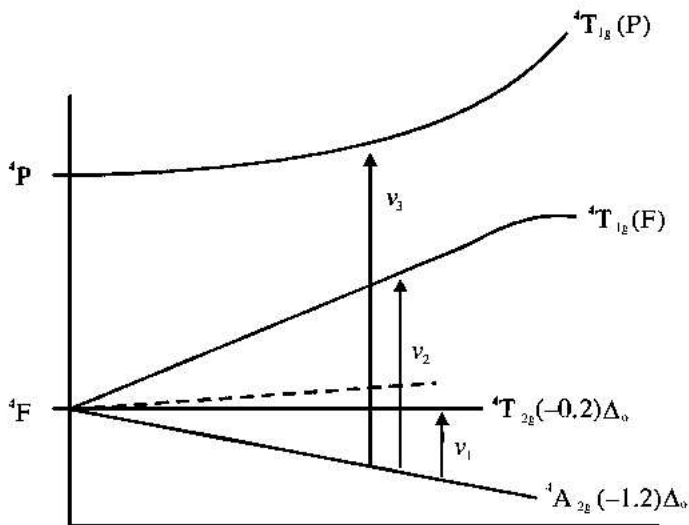
$$2S + 1 = 3$$

Ground state term for  $\text{Ni}^{2+}$  is  ${}^3A_{2g}$

So,  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  transition is observed in  $\text{Ni}^{2+}$  complex

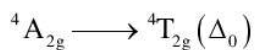
19.Sol.  $[\text{CrF}_6]^{3-} \Rightarrow d^3$

Orgel diagram for  $d^3$



= ground state =  ${}^4F$

First excited state =  ${}^4P$



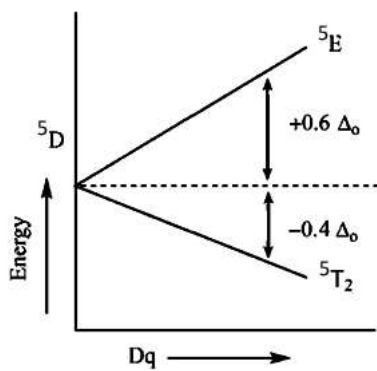
$$\nu_1 \approx 14900 \text{ cm}^{-1}; \nu_2 = 22700 \text{ cm}^{-1}; \nu_3 = 34400 \text{ cm}^{-1}$$

Since,  ${}^4T_{1g}(P)$  and  ${}^4T_{1g}(F)$  have no fix energy therefore, they will not provide accurate value of  $\Delta_0$ .

Thus, energy difference between  ${}^4A_{2g} \rightarrow {}^4T_{2g} \approx 14900 \text{ cm}^{-1}$  will be correspond to  $\Delta_0$ .

**Correct option is (b)**

20Sol. (c) For a tetrahedral complex, 3 absorption are expected in its electronic spectrum.





# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (20)

- Which series correctly place the ligands in order of increasing nephelauxetic effect?  
(a)  $F^\ominus < CN^\ominus < I^\ominus$       (b)  $I^- < Cl^- < F^-$       (c)  $en < NH_3 < H_2O$       (d)  $I^- < Br^- < CN^-$
- The value of B is smaller for the complex than its free ion it is due to  
(a) Jahn – Teller distortion  
(b) delocalisation of the metal electrons over molecules orbital  
(c) high lattice energy  
(d) high value of hydration energy
- The value of Racah parameter B is lower for  $[Co(CN)_6]^{3-}$  than  $[Co(NH_3)_6]^{3+}$  this is due to  
(a) because CN is soft ligand in comparison to  $NH_3$   
(b) because Nephelauxetic effect is higher for  $[Co(CN)_6]^{3-}$ .  
(c) because in case of  $[Co(NH_3)_6]^{3+}$  delocalisation is more in comparison to  $[Co(CN)_6]^{3-}$   
(d) All of these
- Choose the correct statements about Tanabe-Sugano diagrams:  
A. E/B is plotted against  $\Delta_0/B$ .  
B. The zero energy is taken as that of the lowest term.  
C. Terms of the same symmetry cross each other.  
D. Two terms of the same symmetry upon increase of ligand field strength bend apart from each other.  
Correct answer is  
(a) A and B      (b) A and C      (c) A, B and D      (d) A, B, C and D
- Which parameter is used to evaluate the difference in energy of term having different multiplicity.  
(a) B      (b) B and C      (c) A and B      (d) C
- When one of the ethylenediamine ligand of  $[Cr(en)_3]^{3+}$  is replaced with two  $F^\ominus$  ligand to give trans –  $[Cr(en)_2F_2]^+$  how many transition are now expected instead of three.  
(a) 4      (b) 5      (c) 6      (d) 7

7. The complex  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  has very light pink colour. The best reason for it
- The complex does not have a charge transfer transition
  - d-d transitions here are orbital forbidden but spin allowed.
  - d-d transitions here are orbital allowed but spin forbidden.
  - d-d transitions here are both orbital forbidden and spin forbidden.
8. For low spin  $\text{Co}^{3+}$  complexes the possible spin allowed transitions are
- ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$  ;  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$
  - ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$  ;  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$
  - ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  ;  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$
  - ${}^1\text{B}_{1g} \rightarrow {}^1\text{B}_{2g}$  ;  ${}^1\text{B}_{1g} \rightarrow {}^1\text{T}_{1g}$
9. In the absorption spectra of  $[\text{Co}(\text{en})_3]^{3+}$  the two band are observed at:
- $21550 \text{ cm}^{-1}$  and  $31000 \text{ cm}^{-1}$
  - $25000 \text{ cm}^{-1}$  and  $38000 \text{ cm}^{-1}$
  - $31000 \text{ cm}^{-1}$  and  $21000 \text{ cm}^{-1}$
  - $21,550 \text{ cm}^{-1}$  and  $29,600 \text{ cm}^{-1}$
10. In the electronic absorption spectrum of an aqueous solution of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , a very weak band is observed between the bands due to the transitions  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ . The transition responsible for the very weak band is
- (Given: atomic number of Ni is 28)
- ${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{1g}$
  - ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$
  - ${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{2g}$
  - ${}^3\text{A}_{2g} \rightarrow {}^1\text{A}_{2g}$
11. The number of d – d transition(s) expected for the complex  $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$  is
- 1
  - 2
  - 3
  - 4
12. The electronic absorption spectrum of an aqueous solution of  $[\text{Ni}(\text{en})_3]^{2+}$  exhibits broad absorption with  $\lambda_{\text{max}} \approx 325, 550$  and  $900 \text{ nm}$ . The transition corresponding to these bands are
- ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$
  - ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$
  - ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$
  - ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ ,  ${}^3\text{T}_{1g} \rightarrow {}^3\text{A}_{2g}$
13. Arrange the following complexes in increasing order of nephelauxetic parameter.
- $\text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{CN}^- < \text{I}^-$
  - $\text{I}^- < \text{CN}^- < \text{en} < \text{NH}_3 < \text{H}_2\text{O} < \text{F}^-$
  - $\text{CN}^- < \text{I}^- < \text{en} < \text{H}_2\text{O} < \text{NH}_3 < \text{F}^-$
  - $\text{I}^- < \text{en} < \text{NH}_3 < \text{H}_2\text{O} < \text{CN}^- < \text{F}^-$

14. The absorption spectrum of  $[\text{Ti}(\text{OH}_2)_6]^{2+}$  exhibits a band with  $\lambda_{\text{max}} = 510 \text{ nm}$ . What colour of light is absorbed.  
 (a) Green (b) Violet (c) Yellow (d) Blue
15. Which of the following statements are true for nephelauxetic effect.  
 (a) Nephelauxetic parameter  $\beta$  is given by  

$$\frac{B_o - B}{B_o} \approx h_{\text{ligand}} \times k_{\text{metal ion}}$$
  
 (b) The interelectronic repulsion decreases on going from gaseous  $\text{Rh}^{3+}$  ion to  $[\text{Rh}(\text{NH}_3)_6]^{3+}$ .  
 (c) The interelectronic repulsion increases on going from gaseous  $\text{Fe}^{3+}$  ion to  $[\text{FeF}_6]^{3-}$ .  
 (d) All of these
16. Value of the Racah parameter B for free gaseous  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  ions 918, 960 and  $1041 \text{ cm}^{-1}$  respectively. For the corresponding hexa aqua ions, value of B are 725, 835 and  $940 \text{ cm}^{-1}$ . On the basis of above information which of the following statements are true.  
 (a) Here Racah parameter B provide information about electron-electron repulsions.  
 (b) During complex formation electron – electron repulsion increases.  
 (c) During complex formation there is an effective expansion of ‘metal’ orbitals associated with metal ligand bond formation.  
 (d) All of these
17. Estimate the reduction in the interelectronic repulsion in going from gaseous  $\text{Fe}^{3+}$  ion to  $[\text{FeF}_6]^{3-}$ . Given that  $k = 0.24$ ,  $h$  value for  $(6 \text{ F}^-)$  is 0.8.

### ANSWER KEY

- |     |       |     |       |     |       |     |     |     |     |     |     |     |     |
|-----|-------|-----|-------|-----|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (a)   | 2.  | (b)   | 3.  | (a)   | 4.  | (c) | 5.  | (b) | 6.  | (c) | 7.  | (d) |
| 8.  | (b)   | 9.  | (d)   | 10. | (b)   | 11. | (c) | 12. | (a) | 13. | (b) | 14. | (a) |
| 15. | (a,b) | 16. | (a,c) | 17. | (19%) |     |     |     |     |     |     |     |     |



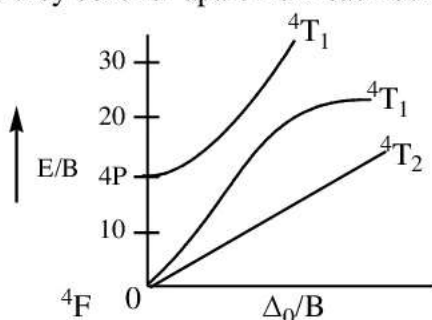
## HINTS & SOLUTION

- 1.Sol.** As the softness of ligand increases nephelauxetic effect increases.  
So, order  $F^{\ominus} < CN^{\ominus} < I^{\ominus}$  is correct.
- 2.Sol.** When free metal ion binds with ligand the average inter electronic repulsion is reduced due to delocalisation of the metal electrons over molecular orbitals, value of B decreases and this phenomenon is known as nephelauxetic effect.
- 3.Sol.** In case of  $[Co(CN)_6]^{3-}$  there is more expansion of cloud and inter electronic repulsion decreases as  $CN^{\ominus}$  is soft in comparison to  $NH_3$  so, more covalent character increase in case of  $CN^{\ominus}$  and B value decreases.

**Tanabe-Sugano** are useful in interpretation of spectra of both high spin and low spin complexes of  $d^2$ - $d^8$  metal cation.

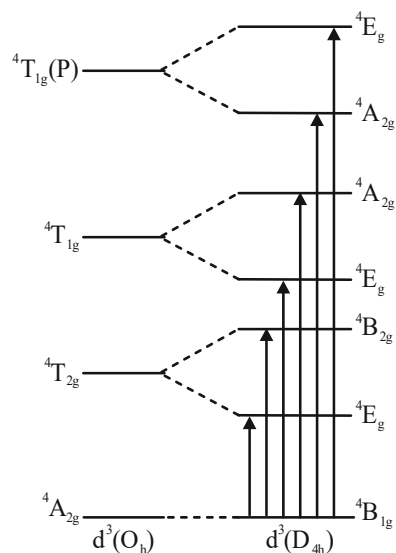
- 4.Sol.** In Tanabe-Sugano, the energy of excited state (expressed as  $E/B$ ) are plotted against ligand field strength (expressed as  $(\Delta_0 / B)$ ).  
Zero energy is taken for the lowest term and also two term of same symmetry never cross each other

and they bent for apart from each other due to repulsion.

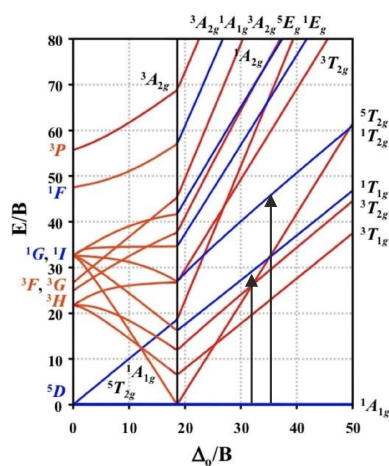


**Correct option is (c)**

- 5.Sol.** In case of different multiplicity both parameter B and C are required to calculate energy but in case of same multiplicity only parameter B is used to calculate energy.



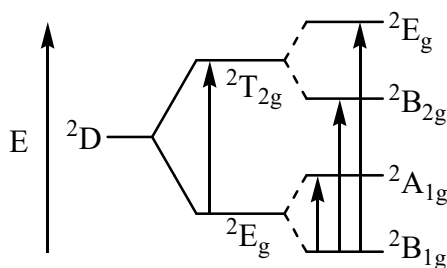
7.Sol. (d)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  Laporte forbidden, Spin forbidden  
 $d^5$



**8.Sol.**

**9.Sol.** In low spin complex  $[\text{Co}(\text{en})_3]^{3+}$  two bands due to transition from  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$  are observed at  $21,550\text{ cm}^{-1}$  and  $29,600\text{ cm}^{-1}$  respectively.

11.Sol.  $[\text{Cu}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$   
 $\text{Cu}^{2+} = d^9$



one transition  ${}^2E_g \rightarrow {}^2T_{2g}$ .

But due to Jahn Teller distortion  ${}^2E_g$  splits into  $B_{1g}$  (lower energy) and  $A_{1g}$  (Higher energy) and  ${}^2T_{2g}$  splits into  $B_{2g}$  and  $E_g$ .

Now transition occur from  $B_{1g}$  to the  $A_{1g}$ ,  $B_{2g}$  or the  $E_g$  states.

Hence: If consider Jahn Teller distortion then expected d - d transition is 3.

If not consider Jahn Teller distortion then d - d transition is 1.

**12.Sol.**  $[\text{Ni}(\text{en})_3]^{2+}$  is a Ni(II),  $d^8$  complex. From the Orgel diagram the three transitions can be assigned; lowest wavelength corresponds to highest energy transition:

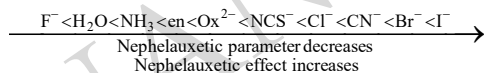
900 nm assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$

550 nm assigned to  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$

325 nm assigned to  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$

Visible region shows  $\approx 400 - 750$  nm, so only 550 nm absorption falls in this range. The band at 325 nm may falls into visible region.

**13.Sol.** Nephelauxetic parameter  $\propto \frac{1}{\text{Nephelauxetic effect}}$



**14.Sol.** As  $\lambda_{\text{max}} = 510$  nm for  $[\text{Ti}(\text{OH}_2)_6]^{2+}$  complex this corresponds to green colour (490 nm – 560 nm).

**15.Sol.** Nephelauxetic parameter is given by  $\frac{B_o - B}{B_o} \approx h_{\text{ligand}} \times k_{\text{metal ion}}$  where h and k are used to parameterize the nephelauxetic series.

As the metal ion bind with ligand electron cloud diffuse and interelectronic repulsion decrease on going from gaseous  $\text{Rh}^{3+}$  to  $[\text{Rh}(\text{NH}_3)_6]^{3+}$

**16.Sol.** Racah parameter provide information about electron electron repulsions. On going from a gaseous metal ion to a metal complex, there is effective expansion of 'metal' orbitals associated with metal – ligand bond formation. This results in a reduction in the electron – electron repulsions and therefore, a reduction in the Racah parameter B.

**17.Sol.**  $\beta = \frac{B_o - B}{B_o} \approx h_{\text{ligand}} \times k_{\text{metal ion}}$

$$= 0.8 \times 0.24$$

$$= 19\%$$



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (21)

- Which has maximum ferromagnetic character?  
(a) Fe (b) Co (c) Ni (d) Pt
- The magnetic moment of complex  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is—  
(a)  $\sqrt{3}$  (b)  $\sqrt{15}$  (c)  $\sqrt{24}$  (d)  $\sqrt{8}$
- $\text{NiBr}_2$  reacts with  $(\text{Et})(\text{Ph})_2\text{P}$  at  $-78^\circ\text{C}$  in  $\text{CS}_2$  to give red compound, 'A' which upon standing at room temperature turns green to give the compound 'B' of the same formula. The measured magnetic moments of 'A' and 'B' are 0.0 & 3.2 B.M respectively. The geometry of 'A' and 'B' are  
(a) Square-planar and Tetrahedral (b) Tetrahedral and Square Planar  
(c) Square-planar and Octahedral (d) Tetrahedral and Octahedral
- The magnetic moment of the complex  $\text{K}_3[\text{CoF}_6]$  is  $5.0 \mu_B$ . The total stabilization energy will be  
(a)  $-0.4\Delta_0$  (b)  $-0.4\Delta_0 + P$  (c)  $-2.4\Delta_0 + 3P$  (d)  $-1.8\Delta_0 + 3P$
- The magnetic moment of  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  corresponding to the presence of  
(a) four unpaired electrons (b) three unpaired electrons  
(c) two unpaired electrons (d) zero unpaired electrons
- Aqueous solution of  $\text{Ni}^{2+}$  contains  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and its magnetic moment is 2.83 BM. When ammonia is added to it, comment on the magnetic moment of solution —  
(a) it will remain same (b) it decreases from 2.838 BM  
(c) it increases from 2.83 BM (d) It cannot be predicted theoretically
- At room temperature, the observed value of  $\mu_{\text{eff}}$  for  $[\text{Cr}(\text{en})_3]\text{Br}_2$  is  $4.75 \mu_B$ . The correct statements about the complex is  
(i) It is a high spin complex (ii) It is a low spin complex  
(iii) It forms octahedral complex (iii) Its hybridisation is  $\text{sp}^3\text{d}^2$   
(a) (i) and (iii) (b) only (ii) (c) (i), (iii) and (iv) (d) (ii), (iii) and (iv)

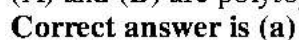
8. A compound with the empirical formula  $\text{Fe}(\text{H}_2\text{O})_4(\text{CN})_2$  has a magnetic moment corresponding to  $2\frac{2}{3}$  unpaired electrons per ion. (Hint: Two octahedral  $\text{Fe}(\text{II})$  species are involved, each containing a single type of ligand. The formula of complex is
- (a)  $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{CN})_6]$  (b)  $[\text{Fe}(\text{H}_2\text{O})_6]_2[\text{Fe}(\text{CN})_6]$   
 (c)  $[\text{Fe}(\text{CN})_6]_2[\text{Fe}(\text{H}_2\text{O})_6]$  (d)  $[\text{Fe}(\text{H}_2\text{O})_6]_3[\text{Fe}(\text{CN})_6]$
9. The orbital contribution to the magnetic moment is quenched in which of the following configuration.
- (a)  $d^2, d^3, d^4$  (high spin),  $d^5$  (high spin)  
 (b)  $d^3, d^2, d^6$  (low spin),  $d^7$  (low spin)  
 (c)  $d^3, d^4$  (high spin),  $d^5$  (high spin),  $d^6$  (low spin)  
 (d)  $d^3, d^4$  (high spin),  $d^5$  (high spin),  $d^6$  (low spin)
10. The calculated and observed magnetic moments differ considerably for an aqua complex of a Lanthanide (III) ion as a result of low lying states of high J. The ion, among the following, is
- (a)  $\text{Ce}^{3+}$  (b)  $\text{Pr}^{3+}$  (c)  $\text{Eu}^{3+}$  (d)  $\text{Yb}^{3+}$
11. The ground state term and magnetic moment of  $\text{Er}^{3+}$  in  $\text{Er}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  complex.
- (a)  ${}^4\text{F}_{15/2}$ , 9.57 BM (b)  ${}^4\text{I}_{15/2}$ , 9.4 BM (c)  ${}^4\text{I}_{9/2}$ , 9.57 BM (d)  ${}^4\text{I}_{15/2}$ , 9.57 BM
12. For second third row d – block element which of the following statements are true.
- (i) spin – orbit coupling is large  
 (ii) spin – orbit coupling is negligible.  
 (iii)  $\mu_{\text{eff}}$  is highly dependent on temperature.  
 (iv)  $\mu_{\text{eff}}$  is independent of temperature.
- (a) (i) and (iii) (b) Only (i) (c) (ii) and (iv) (d) only (iv)
13. Which of the following statements are true for  $\text{Eu}^{3+}$  ion.
- (a) Spin – orbit coupling constant is slightly greater than  $kT$   
 (b) At low temperature the magnetic moment of  $\text{Eu}^{3+}$  approaches to zero.  
 (c) Excited state also contribute to magnetic moment value.  
 (d) All of these
14. Red crystalline  $[\text{NiCl}_2(\text{PPh}_2\text{CH}_2\text{Ph})_2]$  is diamagnetic on heating to 387 K for 2 hours, a blue-green form of the complex is obtained, which has a magnetic moment of  $3.18 m_B$  at 295 K. Identify the correct statement about geometry and magnetic properties of complex.

- (i) Red coloured compound is square planar  
 (ii) Red coloured compound is tetrahedral  
 (iii)  $m_{\text{eff}}$  is greater than  $m_{\text{so}}$  due to orbital contribution.  
 (iv)  $m_{\text{eff}}$  is greater than  $m_{\text{so}}$  due to LS coupling.  
 (a) (i) & (iii)                      (b) (ii) & (iii)                      (c) Only (iii)                      (d) (ii) & (iv)
15.  $[\text{Fe}(\text{dipy})_3](\text{ClO}_4)_3$  complex has a magnetic moment of 2.2 BM. Identify the correct statement.  
 (i) It is inner orbital complex  
 (ii) It is outer orbital complex  
 (iii)  $m_{\text{eff}}$  is greater than  $m_{\text{so}}$   
 (iv) It involve orbital contribution to magnetic moment.  
 (a) (i) and (iii)    (b) (ii), (iii) and (iv)    (c) (i), (iii) and (iv)    (d) Only (ii)
16. In the solid state,  $\text{Co}(\text{py})_2\text{Cl}_2$  is violet and has a magnetic moment of 5.5 BM, but a  $\text{CH}_2\text{Cl}_2$  solution of this compound is blue and has a magnetic moment of 4.42 BM. In contrast,  $\text{Co}(\text{py})_2\text{Br}_2$  is blue in both solid state and in a  $\text{CH}_2\text{Cl}_2$  solution and has magnetic moment of 4.6 BM. Identify the correct statement.  
 (i)  $\text{Co}(\text{py})_2\text{Cl}_2$  will show spin crossover but  $\text{Co}(\text{py})_2\text{Br}_2$  will not show spin crossover  
 (ii) Geometry of violet complex is octahedral  
 (iii) In blue coloured complex orbital contribution to magnetic moment is observed.  
 (iv) In violet coloured complex orbital contribution is observed.  
 (a) only (i)    (b) (ii) and (iv)    (c) (ii) and (iii)    (d) (i), (ii), (iii) and (iv)
17. Moss Bauer spectrum of complex  $[\text{Fe}(\text{1, 10-phenanthroline})_2 - (\text{NCS})_2]$  shows two lines at 300K, four lines at 186 K and again two lines at 77K. This can be attributed to  
 (A) change in the co-ordination mode of NCS  
 (B) Change in spin state of Fe  
 (C) Cis-trans isomerisation  
 (D) Change in metal ligand bond distances  
 The correct statements are  
 (a) A and B                      (b) B and C                      (c) A and C                      (d) B & D

18. The complex  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  (phen = 1.10-phenanthroline) shows spin cross-over behaviour. CFSE and  $\mu_{\text{eff}}$  at 250 and 150 K, respectively are:
- (a)  $0.4 \Delta_0$ , 4.90 BM and  $2.4 \Delta_0$ , 0.00 BM      (b)  $2.4 \Delta_0$ , 2.90 BM and  $0.4 \Delta_0$ , 1.77 BM  
 (c)  $2.4 \Delta_0$ , 0.00 BM and  $0.4 \Delta_0$ , 4.90 BM      (d)  $1.2 \Delta_0$ , 4.90 BM and  $2.4 \Delta_0$ , 0.00 BM
19. What is the value for  $\mu_{\text{eff}}$  for  $[\text{Ni}(\text{en})_3]^{2+}$  taking into account spin-orbit coupling. Given that  $\Delta_{\text{oct}} = 11,500 \text{ cm}^{-1}$  and  $\lambda = -315 \text{ cm}^{-1}$
- (a) 2.83                      (b) 3.14                      (c) 3.83                      (d) 1.73
20. Consider  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  complex having crystal field splitting  $10800 \text{ cm}^{-1}$  and spin-orbit coupling constant  $-315 \text{ cm}^{-1}$ . Based upon above information which of the following statements are true.
- (a) Spin only magnetic moment is 2.83  
 (b)  $\mu_{\text{eff}}$  is greater than also  $\mu_{\text{so}}$  due to orbital contribution  
 (c)  $\mu_{\text{eff}}$  is greater than  $\mu_{\text{so}}$  due to LS coupling.  
 (d)  $\mu_{\text{eff}}$  is less than  $\mu_{\text{so}}$  due to LS coupling.
21. The experimental value of  $\mu_{\text{eff}}$  for complex  $[\text{VCl}_x(\text{bpy})]$  is  $1.77 \mu_{\text{B}}$ . What is the value of x here.

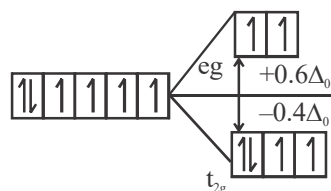
### ANSWER KEY

1.	(a)	2.	(b)	3.	(a)	4.	(a)	5.	(d)	6.	(a)	7.	(c)
8.	(b)	9.	(c)	10.	(c)	11.	(d)	12.	(a)	13.	(d)	14.	(a)
15.	(c)	16.	(b)	17.	(d)	18.	(a)	19.	(b)	20.	(a,c)	21.	(4)


$$\mu = \sqrt{3(3+2)} = \sqrt{15}$$




4.Sol. In  $[\text{CoF}_6]^{3-}$  complex,  $\text{Co}^{+3}$  is a  $d^6$  system with weak field  $\text{F}^-$  ligands to give  $t_{2g}^4 e_g^2$  configuration.



No. of unpaired electrons,  $n = 4$

$$\begin{aligned}\text{CFSE} &= (-0.4 \Delta_0 \times 4) + (0.6 \Delta_0 \times 2) \\ &= -1.6 \Delta_0 + 1.2 \Delta_0 \\ \text{cfse} &= -0.4 \Delta_0\end{aligned}$$

Correct option is (a)

5.Sol.  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  is a low spin  $d^6$  compound, it has zero unpaired electrons.

Correct option is (d)

6.Sol. When  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is formed here ammonia will also behave as weak field ligand as  $\text{H}_2\text{O}$ . So, form high spin complex like  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  so, number of unpaired electron do not change so  $\mu$  will remain same.

7.Sol.  $[\text{Cr}(\text{en})_3]\text{Br}_2$  form octahedral  $[\text{Cr}(\text{en})_3]^{2+}$  complex, and a  $\text{Cr}^{2+}(d^4)$  ion in low spin will have two unpaired electron ( $n = 2$ ) and high – spin, four ( $n = 4$ )

Assume that the spin – only formula is valid (first row metal, octahedral complex):

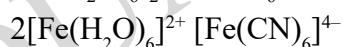
$$\mu(\text{spin – only}) = \sqrt{n(n+2)}$$

$$\text{For low – spin : } \mu(\text{spin – only}) = \sqrt{8} = 2.83$$

$$\text{For high – spin : } \mu(\text{spin – only}) = \sqrt{24} = 4.90$$

The latter is close to the observed value and is consistent with a high-spin complex. So, its hybridisation in case of high spin will be  $sp^3d^2$

8.Sol.  $[\text{Fe}(\text{H}_2\text{O})_6]_2[\text{Fe}(\text{CN})_6]$



$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \rightarrow$  It form high spin complex and has 4 unpaired electron.

$2[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \rightarrow$  So, it will have total 8 unpaired electron.

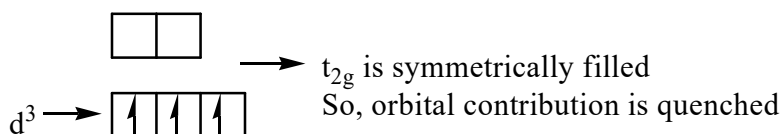
$[\text{Fe}(\text{CN})_6]^{4-} \rightarrow$  Has no unpaired electron.

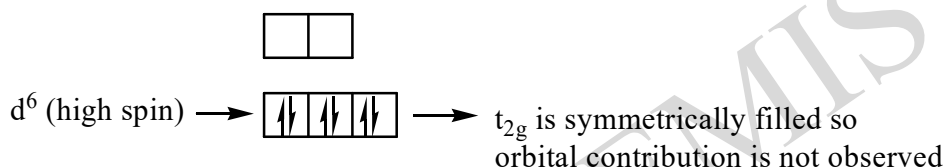
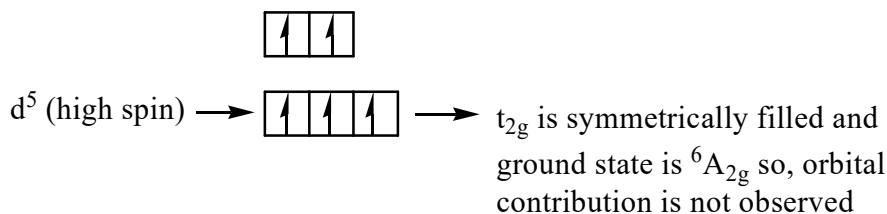
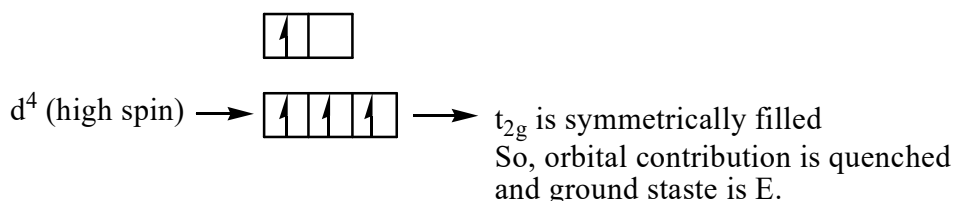
So, 3Fe ions have total 8 unpaired electron

Therefore, per ion there are  $8/3$  electrons

Hence complex is  $[\text{Fe}(\text{H}_2\text{O})_6]_2[\text{Fe}(\text{CN})_6]$

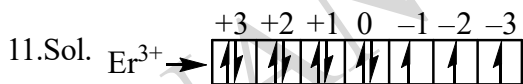
9Sol. Orbital contribution to the magnetic moment is quenched in the complex having A or E ground state and when  $t_{2g}$  is not unsymmetrically filled.





10Sol. (c) Calculated and observed magnetic moments of  $\text{Eu}^{3+}$  ion differ considerably for an aqua complex of a lanthanide (III) ion.

The reason is that with  $\text{Eu}^{3+}$ , the spin orbit coupling constant is only about  $300 \text{ cm}^{-1}$ , which means the difference in energy between the ground state and next excited state is small. Thus, the energy of thermal motion is sufficient to promote some electrons and partially populate the higher state. Measuring the magnetic moment at a low temperature prevents the population of higher energy level. Hence, for  $\text{Eu}^{3+}$  ion, calculated magnetic moment is zero while observed magnetic moment is 3.4-3.6 BM.



$$L = (3 \times 2) + (2 \times 2) + (2 \times 1) + (0 \times 2) - 1 - 2 - 3$$

$$= 6 + 4 + 2 - 6 = 6$$

$$L = 6$$

$$S = 3 \times \frac{1}{2} = \frac{3}{2} \quad 2S+1 = 2 \times \frac{3}{2} + 1$$

$$L+S = 6 + \frac{3}{2} \quad L-S = 6 - \frac{3}{2}$$

$$= \frac{12+3}{2} = \frac{15}{2} \quad \frac{12-3}{2} = \frac{9}{2}$$

More than half filled so, consider higher value of J

$J = 15/2$  so, ground state term is  ${}^4I_{15/2}$ .

To calculate  $\mu = g\sqrt{J(J+1)}$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = 1 + \frac{\frac{15}{2}\left(\frac{15}{2}+1\right) + \frac{3}{2}\left(\frac{3}{2}+1\right) - 6(6+1)}{2\left(\frac{15}{2}\right)\left(\frac{15}{2}+1\right)}$$

$$= 1 + \frac{\frac{15}{2} \times \frac{17}{2} + \frac{3}{2} \times \frac{5}{2} - 6 \times 7}{15\left(\frac{17}{2}\right)} = 1 + \frac{\frac{225+15}{2} - 42}{\frac{15 \times 17}{2}} = 1 + \frac{\frac{135}{2} - 42}{\frac{15 \times 17}{2}} = 1 + \frac{135 - 84}{2} \times \frac{2}{15 \times 17}$$

$$= 1 + \frac{15}{255} = \boxed{1.2}$$

$$\mu = 1.2 \sqrt{J(J+1)} = 1.2 \sqrt{\frac{15}{2}\left(\frac{15}{2}+1\right)} = 1.2 \sqrt{\frac{15}{2} \times \frac{17}{2}}$$

$$= 1.2 \times 7.984 = 9.57 \text{ BM}$$

12.Sol. For second and third d – block metal ions where spin – orbit coupling is large,  $\mu_{\text{eff}}$  is highly dependent on T.

13.Sol. In case of  $\text{Eu}^{3+}$  ion spin orbit coupling constant  $\lambda$  is slightly greater than  $kT$  so, excited state also, contribute to magnetic moment value and  $\mu_{\text{eff}}$  is greater than expected. But at low temperature excited state do not contribute and  $\mu = 0$

14.Sol.  $[\text{NiCl}_2(\text{PPh}_2\text{CH}_2\text{Ph})_2]$        $[\text{NiCl}_2(\text{PPh}_2\text{CH}_2\text{Ph})_2]$

(Red)

(Blue - green)

$\bar{\mu} = 0 \text{ BM}$

$\bar{\mu} = 1.38 \text{ BM}$

diamagnetic

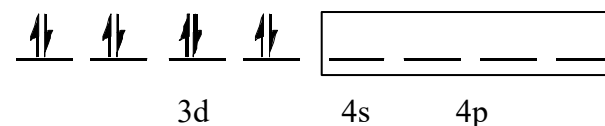
$$\mu = \sqrt{n(n+2)}$$

$$= \sqrt{2(2+2)}$$

$$= \sqrt{8}$$

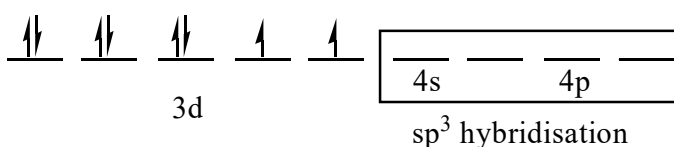
$$m_{\text{SO}} = 2.828$$

$\text{Ni}^{2+} = 3d^8 4s^0 4p^0 =$

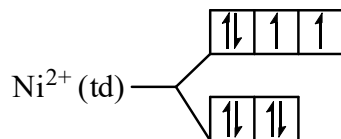


$\text{dsp}^2$  hybridisation (square planar)

For Blue-green  $\text{Ni}^{2+}$  complex



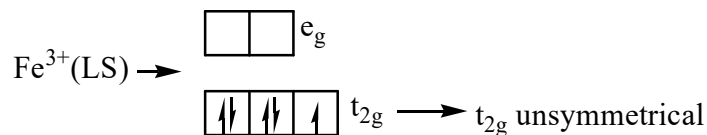
and it will be tetrahedral and will be paramagnetic due to unpaired electron



as  $t_2$  is unsymmetrically filled so, there will be orbital contribution to magnetic moment and  $m_{\text{eff}} > m_{\text{SO}}$ .

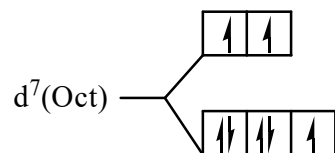
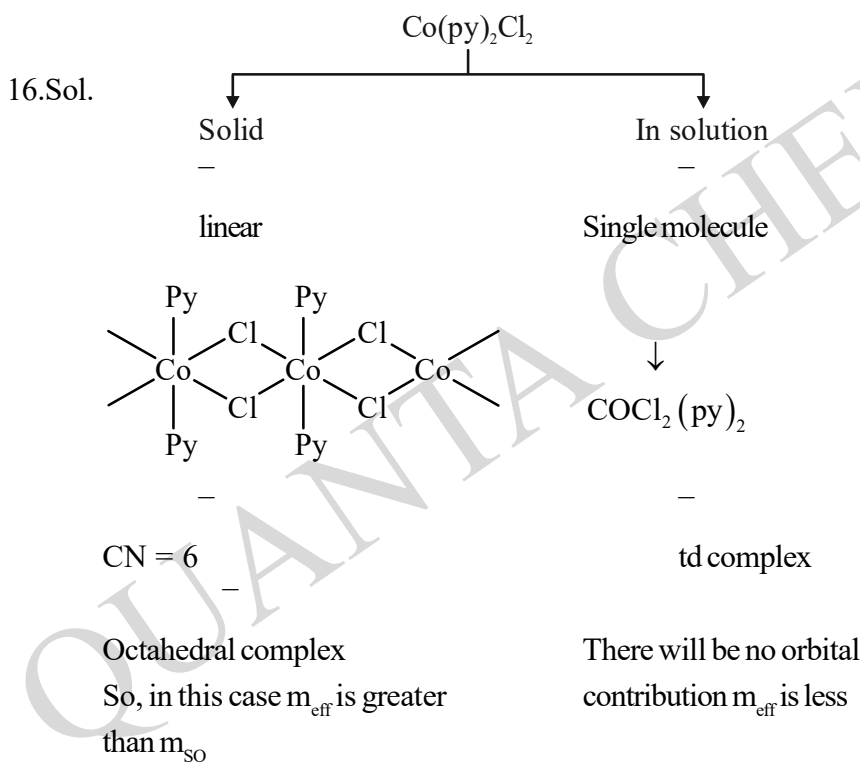
15.Sol.  $[\text{Fe}(\text{dipy})_3](\text{ClO}_4)_3$

In this complex iron is in +3 oxidation state dipy act as strong field ligand.



So, it involved orbital contribution to magnetic moment and inner orbital complex.

Due to orbital contribution  $m_{\text{eff}}$  will be greater than  $m_{\text{SO}}$ .



In case of  $[\text{Co}(\text{Py})_2\text{Br}_2]$  it will exist in CN = 4.

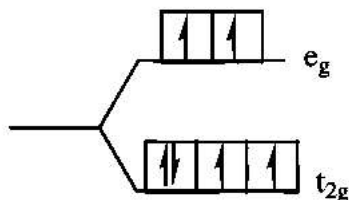
So, in this case also no orbital contribution is observed and it does not form CN = 6 linear chain like structure.

17.Sol. Correct option is (d)

18.Sol.  $[\text{Fe}(\text{Phen})_2(\text{NCS})_2]$

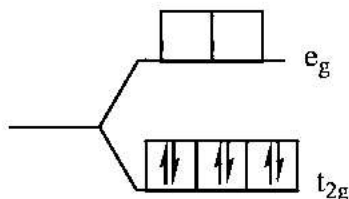
$\text{Fe}^{2+} \Rightarrow d^6$  complex

At high temperature high spin and at low temperature low spin behaviour at 250 K.



$$\text{CFSE} = -1.6\Delta_0 + 1.2\Delta_0 = -0.4\Delta_0$$

$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} \approx 4.90 \text{ BM at 150 K}$$



$$\text{CFSE} = -0.4 \times 6\Delta_0 = -2.4\Delta_0$$

$$\mu = 0$$

**Correct option is (a)**

19.Sol.  $\mu_{\text{eff}} = \mu_{(\text{spin only})} \left( 1 - \frac{4\lambda}{\Delta_{\text{oct}}} \right)$

$$\mu_{\text{spin only}} = \sqrt{n(n+2)} = \sqrt{8} = 2.83$$

$$\mu_{\text{eff}} = 2.83 \left( 1 + \frac{4 \times 315}{11500} \right) = 3.14 \mu_B$$

20. Sol.  $\text{Ni}^{2+}$  has  $d^8$  configuration with 2 unpaired electrons

$$\mu_{\text{so}} = \sqrt{n(n+2)}$$

$$= \sqrt{2(2+2)} = \sqrt{8} = 2.83$$

$\mu_{\text{eff}}$  is greater than  $\mu_{\text{so}}$  due to LS coupling

$$\mu_{\text{eff}} = \mu_{\text{so}} \left( 1 - \frac{4\lambda}{\Delta_{\text{oct}}} \right)$$

$$= 2.83 \left( 1 + \frac{4 \times 315}{10800} \right)$$
$$= 3.16 \mu_B$$

**21.Sol.**  $[\text{VCl}_x(\text{bpy})]$  has 1 unpaired electron;  $d^1$  corresponds to V(IV), therefore  $x = 4$ .

QUANTA CHEMISTRY



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

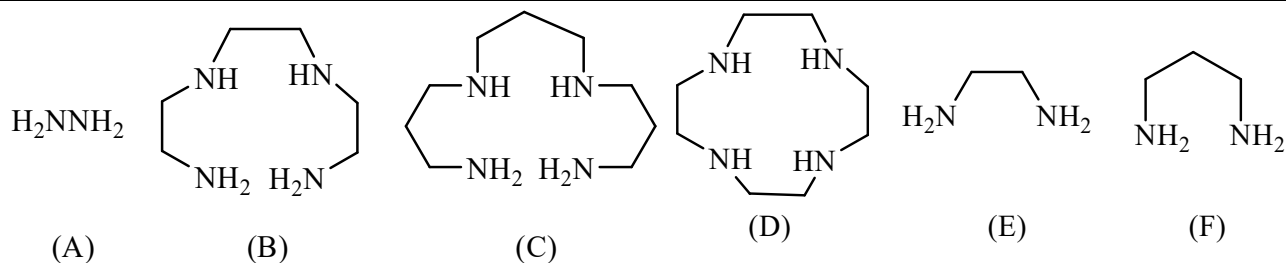
CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (22)

- Correct order for the stability of following complexes is
  - $\text{Co}(\text{NH}_3)_6^{2+} < \text{Ni}(\text{NH}_3)_6^{2+} < \text{Cu}(\text{NH}_3)_6^{2+}$
  - $\text{Co}(\text{NH}_3)_6^{2+} < \text{Cu}(\text{NH}_3)_6^{2+} < \text{Ni}(\text{NH}_3)_6^{2+}$
  - $\text{Cu}(\text{NH}_3)_6^{2+} < \text{Ni}(\text{NH}_3)_6^{2+} < \text{Co}(\text{NH}_3)_6^{2+}$
  - $\text{Ni}(\text{NH}_3)_6^{2+} < \text{Cu}(\text{NH}_3)_6^{2+} < \text{Co}(\text{NH}_3)_6^{2+}$
- The Correct statement regarding the thermodynamic stability and kinetic reactivity of metal ion complexes is that
  - more stable complexes are less reactive
  - there exists a dependence on the bulkiness of the ligand
  - there exists no direct relation between these two phenomenon
  - there exists a dependence on the size of the metal ion
- The correct order of the soft character (as per HSAB Principle) of the central metal ion is
  - $[\text{CrO}_4]^{2-} < [\text{CrCl}_4]^- < [\text{Cr}(\text{bipy})_3] < [\text{Cr}(\text{CO})_5]^{2-}$
  - $[\text{CrCl}_4]^- < [\text{Cr}(\text{bipy})_3] < [\text{CrO}_4]^{2-} < [\text{Cr}(\text{CO})_5]^{2-}$
  - $[\text{CrO}_4]^{2-} < [\text{Cr}(\text{bipy})_3] < [\text{Cr}(\text{CO})_5]^{2-} < [\text{CrCl}_4]^-$
  - $[\text{CrCl}_4]^- < [\text{CrO}_4]^{2-} < [\text{Cr}(\text{CO})_5]^{2-} < [\text{Cr}(\text{bipy})_3]$
- The correct statement with respect to the bonding of the ligands,  $\text{Me}_3\text{N}$  and  $\text{Me}_3\text{P}$  with the metal ions  $\text{Be}^{2+}$  and  $\text{Pd}^{2+}$  is,
  - The ligands bind equally strong with both the metal ions as they are dicationic
  - The ligands bind equally strong with both the metal ions as both the ligands are pyramidal
  - The binding is stronger for  $\text{Me}_3\text{N}$  with  $\text{Be}^{2+}$  and  $\text{Me}_3\text{P}$  with  $\text{Pd}^{2+}$
  - The binding is stronger for  $\text{Me}_3\text{N}$  with  $\text{Pd}^{2+}$  and  $\text{Me}_3\text{P}$  with  $\text{Be}^{2+}$
- Chelate effect is
  - predominantly due to enthalpy change
  - predominantly due to entropy change
  - due to equal contribution of entropy and enthalpy change

- (d) None of these
6. The stepwise formation constants for complexes of  $\text{NH}_3$  with  $[\text{Cu}(\text{OH}_2)_6]^{2+}(\text{aq})$  are  $\log k_{f_1} = 4.15, \log k_{f_2} = 3.5, \log k_{f_3} = 2.89, \log k_{f_4} = 2.13$  and  $\log k_{f_5} = -0.52$ .  $k_{f_5}$  is so different due to:-
- (a) Isomerised product is obtained (b) Increase in coordination number take place  
(c) Decrease in coordination number take place (d) tetrahedral complex is obtained.
7. According to Irving-Williams series, the number of d electrons for the first row transition metal (M) ion having the highest overall stability constant ( $\log b$ ) for  $[\text{M}(\text{EDTA})]^{2-}$  is \_\_\_\_\_
8. Coordinated water molecules of a Cd(II) complex can be successively replaced by  $\text{Br}^-$  finally to result in  $[\text{CdBr}_4]^{2-}$ . In this process, the fourth equilibrium constant is observed to be higher than the third one, because
- (a) equilibrium constant for the last step is always the highest  
(b) three molecules of  $\text{H}_2\text{O}$  are released during the fourth step  
(c) the aqua-Cd(II) species is a octahedral  
(d) an anion ( $\text{Br}^-$ ) replaces a neutral ( $\text{H}_2\text{O}$ ) molecule from the coordination sphere
9. The successive formation constants of Cadmium with  $\text{Br}^-$  are  $K_{f_1} = 36.6, K_{f_2} = 3.47, K_{f_3} = 1.15, K_{f_4} = 2.34$ .  $K_{f_4}$  is greater than  $K_{f_3}$  this is due to
- (i) Enthalpy increases in last step.  
(ii) Due to structural change  
(iii) increase in entropy
- (a) (i) and (ii) (b) (ii) & (iii) (c) Only (ii) (d) (i), (ii) & (iii)
10. The Stepwise stability constant in aqueous solution at  $25^\circ\text{C}$  for the formation of the ions  $[\text{M}(\text{en})(\text{H}_2\text{O})_4]^{2+}$ ,  $[\text{M}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{M}(\text{en})_3]^{2+}$  for copper and Nickel are calculate. Which of the following statments are correct for given complexes.
- (i) Stepwise stability constant for formation of  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  is more than  $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$   
(ii) Stepwise stability constant for formation of  $[\text{Cu}(\text{en})_3]^{2+}$  is more than  $[\text{Ni}(\text{en})_3]^{2+}$   
(iii)  $[\text{Cu}(\text{en})(\text{H}_2\text{O})_4]^{2+}$  is more stable than  $[\text{Ni}(\text{en})(\text{H}_2\text{O})_4]^{2+}$  due to Jahn-Teller distortion.
- (a) (i) and (iii) (b) only (iii) (c) (i) and (ii) (d) (i), (ii) and (iii)
11. Arrange the following ligand in order of increasing ability to form stable complex.





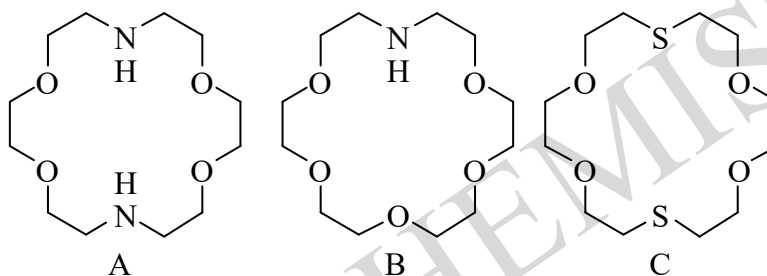
(a)  $D > C > B > F > E > A$

(b)  $D > B > C > E > F > A$

(c)  $D > B > C > F > E > A$

(d)  $D > C > B > E > F > A$

12. The magnitude of the stability constants for  $K^+$  ion complexes of the following supramolecular hosts follows the order,



(a)  $B > A > C$

(b)  $C > A > B$

(c)  $A > B > C$

(d)  $C > B > A$

13. The formation constant for the complexation of  $M^+$  ( $M = Li, Na, K$  and  $Cs$ ) with cryptand, C222 follows the order

(a)  $Li^+ < Cs^+ < Na^+ < K^+$

(b)  $Li^+ < Na^+ < K^+ < Cs^+$

(c)  $K^+ < Cs^+ < Li^+ < Na^+$

(d)  $Cs^+ < K^+ < Li^+ < Na^+$

14. For the given isomers  $[Co(Hdmg)_2(SCN)Py]$  (A) and  $[Co(Hdmg)_2(NCS)Py]$  (B) which of the following statements are true

[Hdmg represents the monanion dimethyl glyoximate.]

(i) A is thermodynamically more stable

(ii) B is thermodynamically more stable

(iii) Its product is formed according to site selection principle.

(iv) Product is formed according to Phenomenon of symbiosis

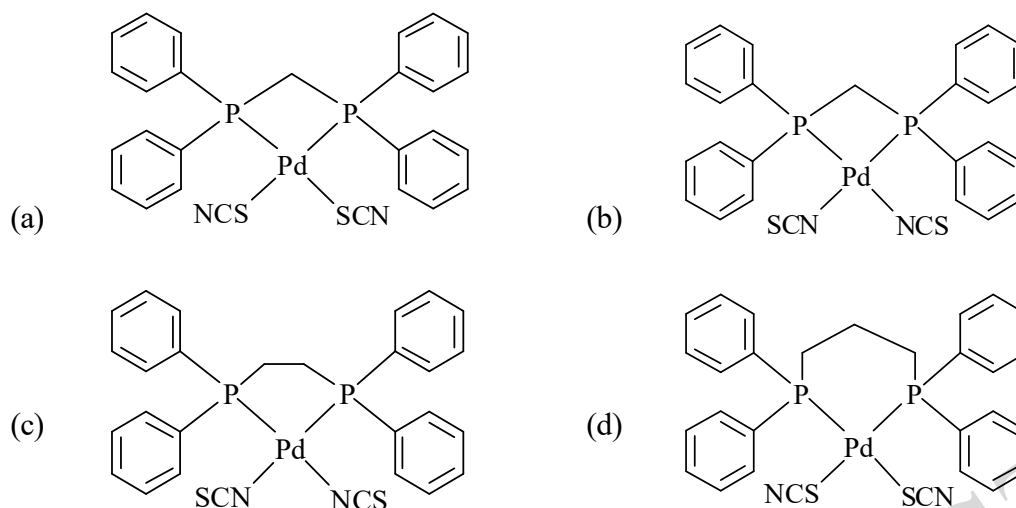
(a) (ii) &amp; (iv)

(b) (ii) &amp; (iii)

(c) (i) &amp; (iii)

(d) (i) &amp; (iv)

15. Considering the ambidentate behaviour of thiocyanate ion, the most stable structure among the following is



16. The macrocyclic ligand enterobactin has an extraordinarily high affinity for  $\text{Fe}^{3+}$  with a stability constant of  $10^{52}$ . This is due to

- (i) Site-selection principle observed in square planar  
 (ii) Symbiosis phenomenon observed in octahedral complex.  
 (iii) Rigid preorganised structure of enterobactin

- (a) (i) & (iii)      (b) (ii) and (iii)    (c) Only (ii)      (d) Only (iii)

17. Among the following complexes correct stability order is :

- (a)  $\text{Cu}(\text{NH}_3)_6^{2+} < \text{Cu}(\text{en})(\text{NH}_3)_4^{2+} < \text{Cu}(\text{en})_2^{2+} < \text{Cu}(\text{en})_3^{2+}$   
 (b)  $\text{Cu}(\text{NH}_3)_6^{2+} < \text{Cu}(\text{en})(\text{NH}_3)_4^{2+} < \text{Cu}(\text{en})_2(\text{NH}_3)_2^{2+} > \text{Cu}(\text{en})_3^{2+}$   
 (c)  $\text{Cu}(\text{NH}_3)_6^{2+} > \text{Cu}(\text{en})(\text{NH}_3)_4^{2+} > \text{Cu}(\text{en})_2(\text{NH}_3)_2^{2+} > \text{Cu}(\text{en})_3^{2+}$   
 (d)  $\text{Cu}(\text{NH}_3)_6^{2+} < \text{Cu}(\text{en})(\text{NH}_3)_4^{2+} < \text{Cu}(\text{en})_2(\text{NH}_3)_2^{2+} < \text{Cu}(\text{en})_3^{2+}$

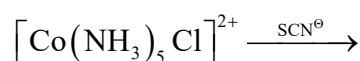
18. The Correct stability order is :

- (a)  $[\text{Ni}(\text{NH}_3)_6]^{2+} > [\text{Ni}(\text{en})_3]^{2+} > [\text{Ni}(\text{EDTA})]^{2-}$     (b)  $[\text{Ni}(\text{en})_3]^{2+} > [\text{Ni}(\text{EDTA})]^{2-} > [\text{Ni}(\text{NH}_3)_6]^{2+}$   
 (c)  $[\text{Ni}(\text{EDTA})]^{2-} > [\text{Ni}(\text{en})_3]^{2+} > [\text{Ni}(\text{NH}_3)_6]^{2+}$     (d)  $[\text{Ni}(\text{EDTA})]^{2-} = [\text{Ni}(\text{en})_3]^{2+} > [\text{Ni}(\text{NH}_3)_6]^{2+}$

19. Product in the following reaction is  $[\text{Co}(\text{CN})_5\text{NCS}]^{3-} \xrightarrow{\Delta} \text{product}$

- (a)  $[\text{Co}(\text{CN})_6]^{3-}$       (b)  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{3-}$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$       (d)  $[\text{Co}(\text{CN})_5\text{SCN}]^{3-}$

20. Complete the following reactions :—



- (a)  $[\text{Co}(\text{NH}_3)_5\text{SCN}]^{2+}$       (b)  $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$   
 (c)  $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{NCS})]^+$       (d)  $[\text{Co}(\text{SCN})_2(\text{NH}_3)_4]^+$

---

**ANSWER KEY**

---

- |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (a) | 2.  | (c) | 3.  | (a) | 4.  | (c) | 5.  | (b) | 6.  | (c) | 7.  | (9) |
| 8.  | (b) | 9.  | (b) | 10. | (a) | 11. | (b) | 12. | (a) | 13. | (a) | 14. | (a) |
| 15. | (a) | 16. | (b) | 17. | (b) | 18. | (c) | 19. | (d) | 20. | (b) |     |     |

QUANTA CHEMISTRY

## HINTS & SOLUTION

- 1Sol. For a given ligand & metals of same oxidation states, stability of the complexes increased with decrease in size of metal cations, so the order of stability of complexes will be—



$$b_n = K_1 \cdot K_2 \cdot K_3 \cdot \dots \cdot K_n$$

- 2Sol. Thermodynamic stability is a measure of the extent to which the complex will form. It depends upon the metal-ligand bond energies, stability constants etc.

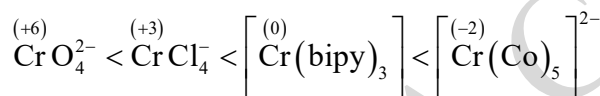
Kinetic reactivity, on the other hand, refers to the speed with which transformations leading to the attainment of equilibrium will occur. It depends upon the activation energy.

Thus, these two, i.e., thermodynamic stability and kinetic reactivity, have no direct relation. (A stable complex may be inert or labile or an inert complex may be stable or unstable).

Correct answer is (c)

- 3Sol. Softness of any species depends upon polarizability of central metal which in turn depends on its oxidation state, therefore

$$\text{Softness} \propto \frac{1}{\text{oxidation state of metal}}$$

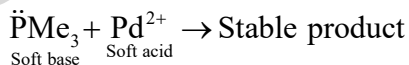
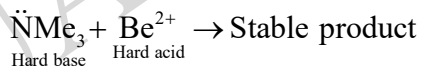


As oxidation state decreases, softness increases.

Correct option is (a)

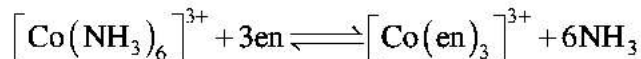
- 4Sol. According to HSAB concept (Pearson theory)

Hard acid has a tendency to combine with hard base in order to give the stable product. Hence bond is stronger.



Correct option is (c)

- 5Sol. Chelate effect is predominately due to entropy change

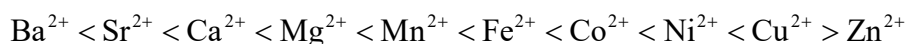


$\Delta H$  nearly same but entropy change is more.

Correct option is (b)

**6.Sol.** The value of the stepwise formation constants drop from 1 to 4, as expected on statistical grounds. However the fifth stepwise formation constant is substantially lower, suggesting a change in coordination. Infact what happen is that square-planar  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion forms and further coordination does not occur.

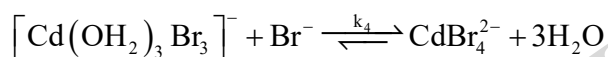
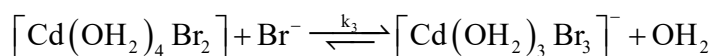
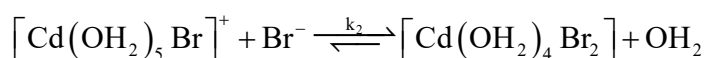
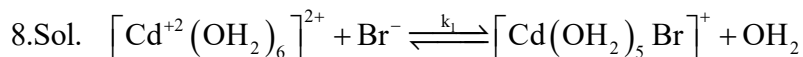
**7.Sol.** (9) For  $\text{M}^{2+}$  ions, the general trend in stability for complexes is,



This trend in stability is known as Irving-Williams series.

Hence,  $\text{Cu}^{2+}$  is more stable than other first row transition metlas.

Therefore, the number of d-electrons for the first transition metal (M), i.e.  $\text{Cu}^{2+}$  ion having the highest overall stability constant (log b) for  $[\text{M}(\text{EDTA})]^{2-}$  is 9.



Step 4 is entropically driven due to decrease in coordination number from 6 to 4 which increases number

**9.Sol.** The anomaly suggests a structural change, so we need to consider what is might be Aqua complex are usually six-coordinate whereas halogen complexes of  $\text{M}^{2+}$  ions are commonly tetrahedral.

The reaction of the complex with three  $\text{Br}^-$  group to add the fourth is



This step is favoured by the release of three  $\text{H}_2\text{O}$  molecules from the relatively restricted coordination sphere environment.

This is entropically driven. of product molecules and consequently  $k_4 > k_3$  (which does not enjoy such entropy benefits).

Correct option is (b)

**10.Sol.** Jahn Teller distortion increase the thermodynamic stability of complex.

The stepwise stability constant for  $[\text{Cu}(\text{en})(\text{H}_2\text{O})_4]^{2+}$  and  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  are more than  $[\text{Ni}(\text{en})(\text{H}_2\text{O})_4]^{2+}$  and  $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_4]^{2+}$  due to Jahn-Teller distortion observed in  $\text{Cu}^{2+}$  complex.

But in last step bad chelation is observed. So, stability constant for  $[\text{Ni}(\text{en})_3]^{2+}$  is more stable than  $[\text{Cu}(\text{en})_3]^{2+}$

**11.Sol.** Metal complex of polydentate ligands are significantly more stable than similar monodentate ligand due to increase in entropy. Five membered chelate rings, are significantly more stable than complex with six membered chelate rings.

**12.Sol.** As the given metal is hard so it will bind strongly with oxygen then nitrogen

Binding order:  $\text{O} > \text{N} > \text{S}$

Correct answer is (a)

- 13.Sol. The stability (formation constant for complexation of cryptate complex depends upon)  
 (1) size of cavity  
 (2) size of metal cation

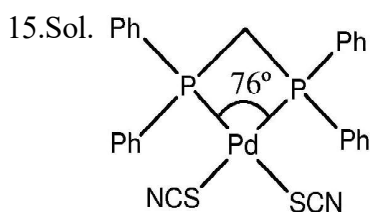
cryptand	suitable cation
crypt – 211	$\text{Li}^+$
crypt – 221	$\text{Na}^+$
crypt – 222	$\text{K}^+$

Hence,  $\text{K}^+$  ion will form most stable complex with cryptand-222.

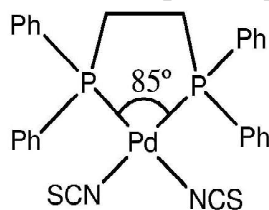
**Correct option is (a)**

- 14.Sol.  $\text{Co}^{3+}$  ion is attached to Hdmg ligand which is bidentate ligand through N which is a hard centre and if ligand NCS is attached to this complex it will also form a stable complex with N terminal according to the Phenomenon symbiosis observed in octahedral complex.

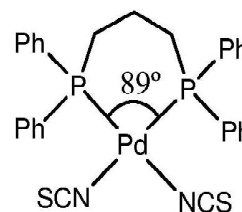
So, isomer B is more stable.



Small P–Pd–P angle, less steric hindrance effective  $\pi$  Pd–SCN<sup>–</sup> bonding



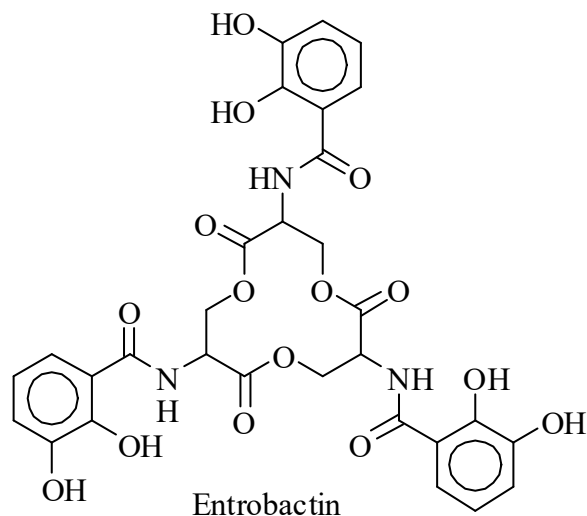
Increase in P–Pd–P angle, increase in steric hindrance. No effective  $\pi$  bonding from the P atom, the S atom of SCN<sup>–</sup> ligand can form  $\pi$  bond but due to steric hindrance SCN<sup>–</sup> binds through N atom.



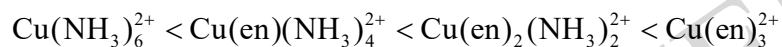
P–Pd–P bond angle, further increase with increase in size of chelate ring and hence steric hindrance increases. No effective  $\pi$  bonding from P, the S atom of SCN<sup>–</sup> can form the  $\pi$  bond but steric hindrance favours the Pd–N bonding

**Correct option is (a)**

- 16.Sol. The three catechol group are attached to triserine ring to form a preorganised rigid structure and  $\text{Fe}^{3+}$  has correct size and charge to form a very stable complex with this preorganised enterobactin ligand.

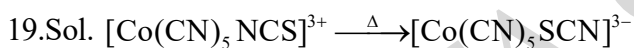


17.Sol: The correct stability order is

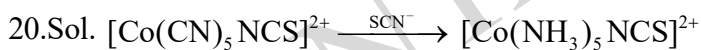


because in  $[\text{Cu}(\text{en})_3]^{2+}$  Jahn Teller distortion brings strain into ethylene diamine more than is added along z-axis and in other complexes chelating ligands form more stable complexes than the analogous monodentate ligands.

18.Sol. As EDTA is hexadentate chelating ligand and formation of this complex is entropically more favourable. Therefore correct option is (c)



this complex will be formed due to linkage isomers formation of isothiocyanato thiocyanato.



in this complex ammonia tend to harder the cobalt and so the thiocyanate bonds preferentially through the nitrogen atom.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (23)

- The water exchange rates for the complex ions follow the order
  - $[\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+} > [\text{V}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- The rate of exchange of  $\text{OH}_2$  present in the coordination sphere by  $^{18}\text{OH}_2$  of (i)  $[\text{Cu}(\text{OH}_2)_6]^{2+}$  (ii)  $[\text{Mn}(\text{OH}_2)_6]^{2+}$ , (iii)  $[\text{Fe}(\text{OH}_2)_6]^{2+}$ , (iv)  $[\text{Ni}(\text{OH}_2)_6]^{2+}$ , follows an order
  - (i) > (ii) > (iii) > (iv)
  - (i) > (iv) > (iii) > (ii)
  - (ii) > (iii) > (iv) > (i)
  - (ii) > (i) > (iv) > (iii)
- The rate of exchange of cyanide ligands in the complexes (i)  $[\text{Ni}(\text{CN})_4]^{2-}$ , (ii)  $[\text{Mn}(\text{CN})_6]^{3-}$  and (iii)  $[\text{Cr}(\text{CN})_6]^{3-}$  by  $^{14}\text{CN}$  follow the order
  - (ii) > (i) > (iii)
  - (iii) > (i) > (ii)
  - (i) > (iii) > (ii)
  - (i) > (ii) > (iii)
- The correct order of the rate of exchange of water molecules between the coordination sphere and the bulk is
  - $\text{Cr}^{3+} < \text{Al}^{3+} < \text{Cr}^{2+} < \text{Ni}^{2+}$
  - $\text{Cr}^{3+} < \text{Al}^{3+} < \text{Ni}^{2+} < \text{Cr}^{2+}$
  - $\text{Cr}^{3+} < \text{Ni}^{2+} < \text{Cr}^{2+} < \text{Al}^{3+}$
  - $\text{Cr}^{3+} < \text{Cr}^{2+} < \text{Al}^{3+} < \text{Ni}^{2+}$
- Designate the following complexes X, Y and Z as inert or labile
$$\text{X} = [\text{Al}(\text{C}_2\text{O}_4)_3]^{3-} \quad \text{Y} = [\text{V}(\text{H}_2\text{O})_6]^{2+} \quad \text{Z} = [\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$$
  - X and Y are inert; Z is labile
  - X and Z are labile; Y is inert
  - X is inert; Y and Z are labile
  - X is labile; Y and Z are inert



6. The relative rates of water exchange for the hydrated complexes of (1)  $\text{Ni}^{2+}$ , (2)  $\text{V}^{2+}$  and (3)  $\text{Cr}^{3+}$  ions follow the trend
- (a)  $(1) > (2) > (3)$       (b)  $(1) < (2) < (3)$       (c)  $(1) > (2) < (3)$       (d)  $(1) < (2) > (3)$
7. High spin  $d^4$  complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  is labile, but the low spin  $d^4$  complex ion  $[\text{Cr}(\text{CN})_6]^{4-}$  is inert this is due to
- (i)  $[\text{Cr}(\text{CN})_6]^{4-}$  from inner orbital complex  
 (ii) Strong JTD is observed in  $[\text{Cr}(\text{CN})_6]^{4-}$   
 (iii) High CFSE of  $[\text{Cr}(\text{CN})_6]^{4-}$  complex  
 (iv)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  from outer orbital complex
- (a) (i) & (ii)      (b) (ii) only      (c) (i), (iii) & (iv)      (d) only (iii)
8. In an observation two separate water exchange rates are found for  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  in aqueous solution. Reason for this observation.
- (a) Due to Jahn – Teller distortion      (b) High hydration energy  
 (c) High lattice energy      (d) because it form outer sphere complex
9. Arrange the following in order of increasing rate of water exchange.
- (a)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Al}(\text{H}_2\text{O})_6]^{3+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$   
 (b)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} > [\text{Al}(\text{H}_2\text{O})_6]^{3+} > [\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$   
 (c)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+} > [\text{Al}(\text{H}_2\text{O})_6]^{3+}$   
 (d)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} > [\text{Al}(\text{H}_2\text{O})_6]^{3+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+} > [\text{V}(\text{H}_2\text{O})_6]^{3+}$
10. Put in order of increasing rate of substitution by  $\text{H}_2\text{O}$  the complex are:-
- (a)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Rh}(\text{NH}_3)_6]^{3+} > [\text{Ir}(\text{NH}_3)_6]^{3+}$   
 (b)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} > [\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Rh}(\text{NH}_3)_6]^{3+} > [\text{Ir}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} > [\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Ir}(\text{NH}_3)_6]^{3+} > [\text{Rh}(\text{NH}_3)_6]^{3+}$   
 (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Mn}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Ir}(\text{NH}_3)_6]^{3+} > [\text{Rh}(\text{NH}_3)_6]^{3+}$

11. For the following complex magnetic moment of the complexes are given below. Identify which of the following complex are labile

 $\mu_{\text{eff}}$ 

I. Ammonium oxopentachlorochromate (V) 1.82

II. Potassium hexaiodomanganate (IV) 3.87

III. Potassium hexacyanoferrate (III) 2.40

IV. Hexa ammine iron(II) chloride 5.42

- (a) I and III                      (b) only IV                      (c) I and IV                      (d) III and IV

12. The usual form of the experimental rate law for substitution in square planer Pt(II) complexes contains two terms:

$$\text{Rate} = k_1[\text{PtL}_3\text{X}] + k_2[\text{PtL}_3\text{X}][\text{Y}]$$

where kinetic  $[\text{PtL}_3\text{X}]$  is the starting complex and Y is the entering group. The reason for the two-term law is that:

- (a) there are competitive associative and dissociative pathways  
 (b) there are two competing dissociative pathways  
 (c) the solvent enters in the rate-determining step, and then two competing fast steps follow  
 (d) the solvent completes with Y in the rate-determining step

13. Which ion is kinetically inert?

- (a)  $\text{Cr}^{2+}$                       (b)  $\text{Co}^{3+}$                       (c)  $\text{Co}^{2+}$                       (d)  $\text{Fe}^{3+}$

14. Which ordering correctly shows the variation in rates of water exchange in high-spin sqa complexes  $[\text{M}(\text{OH}_2)_6]^{n+}$ ?

- (a)  $\text{Co}^{2+} > \text{Cr}^{2+}$                       (b)  $\text{V}^{2+} > \text{Co}^{2+}$                       (c)  $\text{Cr}^{3+} > \text{Fe}^{3+}$                       (d)  $\text{Cr}^{2+} > \text{Cr}^{3+}$

15. The first step in the Eigen-Wilkins mechanism for  $\text{ML}_6$  undergoing Y and L substitution is:

- (a) loss of L  
 (b) addition of Y  
 (c) formation of a weakly bound encounter complex  
 (d) formation of a 7-coordinate complex in the rate-determining step

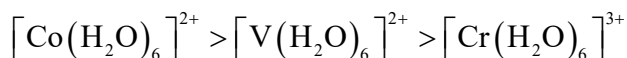
16. Racemization of a chiral complex such as  $[\text{Cr}(\text{ox})_3]^{3-}$  is least likely to occur by:
- a dissociative pathway
  - a pathway involving a 5-coordinate species in which an  $\text{ox}^{2-}$  ligand is monodentate
  - the Ray-dutt twist mechanism
  - the Bailar twist mechanism
17. Three of the following ions are kinetically inert, one is labile. Which ion is labile?
- $\text{Rh}^{3+}$
  - $\text{Ti}^{3+}$
  - $\text{Ru}^{2+}$
  - $\text{Cr}^{3+}$
18. The average residence time of an  $\text{H}_2\text{O}$  molecule in the coordination sphere of  $[\text{Cs}(\text{OH}_2)_8]^+$  is approximately  $10^{-10}\text{s}$ . The value of the water exchange rate constant is therefore:
- $10^{-10}\text{ s}$
  - $10^{10}\text{ s}^{-1}$
  - $10^{-10}\text{ s}^{-1}$
  - $10^{10}\text{ s}$
19. The kinetics of the isomerization of cis to trans  $[\text{Mo}(\text{CO})_4(\text{PEt}_3)_2]$  can be followed by IR spectroscopy which of the following regions of the IR spectrum would you focus on to monitor the reaction?
- $2000 - 1800\text{ cm}^{-1}$
  - $3500 - 3000\text{ cm}^{-1}$
  - $1600 - 1400\text{ cm}^{-1}$
  - $1200 - 800\text{ cm}^{-1}$
20. Which of the following statements are correct.
- Rate of water exchange for the group 1 metal ions vary over a small range from  $[\text{Li}(\text{H}_2\text{O})_6]^+$  (least labile) to  $[\text{Cs}(\text{OH}_2)_8]^+$  (most labile).
  - Rate of water exchange for the group 2 metal ion varies from  $[\text{Be}(\text{OH}_2)_4]^{2+}$  ( $\approx 10^3\text{s}^{-1}$ ) to  $[\text{Ba}(\text{OH}_2)_8]^{2+}$  ( $\approx 10^9\text{s}^{-1}$ )
  - The  $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$  ion lies at slow – exchange extreme limit with  $\tau = 9.1 \times 10^9\text{s} = 290\text{ years}$ .
  - All of these

## ANSWER KEY

- |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (d) | 2.  | (a) | 3.  | (d) | 4.  | (b) | 5.  | (d) | 6.  | (a) | 7.  | (c) |
| 8.  | (a) | 9.  | (a) | 10. | (b) | 11. | (c) | 12. | (d) | 13. | (b) | 14. | (d) |
| 15. | (c) | 16. | (a) | 17. | (b) | 18. | (b) | 19. | (a) | 20. | (d) |     |     |

## HINTS & SOLUTION

1Sol.	<b>Class - I</b>	<b>Class - II</b>	<b>Class - III</b>	<b>Class - IV</b>
	First order exchange rate constants are of the order $10^8 \text{ s}^{-1}$ $\text{Cr}^{+2}, \text{Cu}^{2+}$ $\text{Hg}^{2+}, \text{Gd}^{3+}$ $\text{Ba}^{2+}$ etc.	Rate constant ranges $10^5$ to $10^8 \text{ s}^{-1}$ $\text{Ni}^{2+}, \text{Ti}^{3+}, \text{Mg}^{2+}$ $\text{Co}^{2+}, \text{In}^{3+}$ etc	Rate constant order is of the range 1 to $10^4 \text{ s}^{-1}$ $\text{Al}^{3+}, \text{V}^{2+}, \text{Pd}^{2+},$ $\text{Fe}^{3+}, \text{Be}^{2+}, \text{Ga}^{3+}$ etc	Slowert rate of water exchange $10^{-1}$ to $10^{-9} \text{ s}^{-1}$ $\text{Cr}^{+3}, \text{Ru}^{3+}, \text{Pt}^{2+}$ etc



Correct option is (d)

- 2Sol. The rate of water exchange in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is fastest due to Jahn – Teller distortion. For other three complexes of 3d – series dipositive metal cation. The rate of water exchange decreases with increase in effective nuclear charge and decrease in size.

**Correct answer is (a)**

- 3Sol. Square planar complexes are more labile than six-coordinated complex due to more space for attack of nucleophile

Hence the rate of exchange in  $[\text{Ni}(\text{CN})_4]^{2-}$  is highest.

In octahedral complexes rate of exchange is decided by change in CFSE on going from on to five coordinated intermediate octahedral.

More the positive change in CFSE more will be lability

$[\text{Mn}(\text{CN})_6]^{3-}$ , change is – 0.86

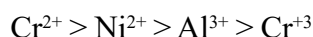
$[\text{Cr}(\text{CN})_6]^{3-}$ , change is –2.00

∴  $[\text{Cr}(\text{CN})_6]^{3-}$  is least labile.

- 4.Sol. Metal ions are classified in four categories based on rate of exchange of coordinated water

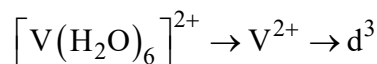
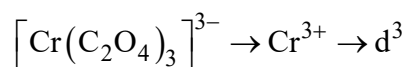
<b>Class - I</b>	<b>Class - II</b>	<b>Class - III</b>	<b>Class - IV</b>
First order exchange rate constants are of the order $10^8 \text{ s}^{-1}$ $\text{Cr}^{+2}, \text{Cu}^{2+}$ $\text{Hg}^{2+}, \text{Gd}^{3+}$ $\text{Ba}^{2+}$ etc.	Rate constant ranges $10^5$ to $10^8 \text{ s}^{-1}$ $\text{Ni}^{2+}, \text{Ti}^{3+}, \text{Mg}^{2+}$ $\text{Co}^{2+}, \text{In}^{3+}$ etc	Rate constant order is of the range 1 to $10^4 \text{ s}^{-1}$ $\text{Al}^{3+}, \text{V}^{2+}, \text{Pd}^{2+},$ $\text{Fe}^{3+}, \text{Be}^{2+}, \text{Ga}^{3+}$ etc	Slowert rate of water exchange $10^{-1}$ to $10^{-9} \text{ s}^{-1}$ $\text{Cr}^{+3}, \text{Ru}^{3+}, \text{Pt}^{2+}$ etc

Correct order of water exchange rates



Correct option is (b)

5.Sol. The complexes having  $d^3$  electronic configuration is most inert complexes.



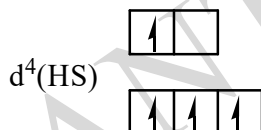
Both are inner orbital complex, there is no low lying vacant d orbital. Hence only Y and Z are inert.

Correct option is (d)

	Class - I	Class - II	Class - III	Class - IV
6.Sol.	First order exchange rate constants are of the order $10^8 \text{ s}^{-1}$ $\text{Cr}^{2+}, \text{Cu}^{2+}$ $\text{Hg}^{2+}, \text{Gd}^{3+}$ $\text{Ba}^{2+}$ etc.	Rate constant ranges $10^5$ to $10^8 \text{ s}^{-1}$ $\text{Ni}^{2+}, \text{Ti}^{3+}, \text{Mg}^{2+}$ $\text{Co}^{2+}, \text{In}^{3+}$ etc	Rate constant order is of the range 1 to $10^4 \text{ s}^{-1}$ $\text{Al}^{3+}, \text{V}^{2+}, \text{Pd}^{2+},$ $\text{Fe}^{3+}, \text{Be}^{2+}, \text{Ga}^{3+}$ etc	Slowest rate of water exchange $10^{-1}$ to $10^{-9} \text{ s}^{-1}$ $\text{Cr}^{3+}, \text{Ru}^{3+}, \text{Pt}^{2+}$ etc

Correct option is (a)

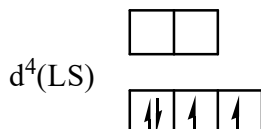
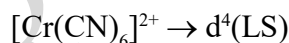
7.Sol.  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} \rightarrow d^4 (\text{HS})$



It is labile as CFSE is low

JTD is also observed

It forms outer orbital complex



It is inert as high CFSE

Inner sphere complex

Lower lying LUMO is absent

8.Sol.  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is a  $d^9$  complex, subject to Jahn – Teller distortion. Therefore different rates are observed for exchange of axial and equatorial water molecules.

9.Sol.  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Al}(\text{H}_2\text{O})_6]^{3+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

10.Sol.  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} > [\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Rh}(\text{NH}_3)_6]^{3+} > [\text{Ir}(\text{NH}_3)_6]^{3+}$

11.Sol. I.  $\text{Cr}^{5+} \rightarrow d^1 \rightarrow \text{Labile}$

$$\mu_{\text{SO}} \sqrt{1(1+2)} = 1.732 \text{ and orbital contribution are also included}$$

II.  $\text{Mn}^{4+} \rightarrow d^3 \rightarrow \text{inert}$

$$\mu_{\text{so}} \sqrt{3(3+2)} = \sqrt{15} = 3.87$$

III.  $\text{Fe}^{3+}$  (LS) as CN is strong field ligand

$d^5$  (LS)  $\rightarrow$  inert

IV.  $\text{Fe}^{2+}$  (HS)  $\rightarrow d^6$  (HS)  $\rightarrow$  Labile

12.Sol. The usual form of the experimental rate law for substitution in square planar Pt(II) complexes contain two terms:

$$\text{Rate} = k_1[\text{PtL}_3\text{X}] + k_2[\text{PtL}_3\text{X}][\text{Y}]$$

Where  $\text{PtL}_3\text{X}$  is the starting complex and Y is the entering group. The reason for two terms in rate law is that the solvent competes with Y in rate determining step.

13.Sol.  $\text{Co}^{3+}$  is kinetically inert.

14.Sol.  $\text{Cr}^{2+}$  is more labile than  $\text{Cr}^{3+}$

15.Sol. In Eigen-Wilkins mechanism firstly a weak bonded encounter complex is formed. 16.Sol.

16.Sol. A dissociative pathway. It has more tendency to show racemization by other three mechanism.

17.Sol.  $\text{Cr}^{3+}(d^3)$  is inert,  $\text{Rh}^{3+}$  and  $\text{Ru}^{2+}$  will form low spin complex are also inert. So, correct option is (b).

18.Sol. Rate constant for water exchange is given by  $= \frac{1}{\text{residence time}} = 10^{10} \text{ s}^{-1}$

19.Sol. Stretching frequency of carbonyl will be mainly observed in region  $2000 - 1800 \text{ cm}^{-1}$ .

20.Sol. All the above statements are correct.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (24)

- The reactions of  $\text{Ni(CO)}_4$  with the ligand L ( $\text{L} = \text{PMe}_3$  or  $\text{P(OMe)}_3$ ) yields  $\text{Ni(CO)}_3\text{L}$ . The reaction is  
(a) Associative                      (b) Dissociative                      (c) Interchange ( $\text{I}_a$ )                      (d) Interchange ( $\text{I}_d$ )
- The rate of the given reaction depends on  
$$\text{Ni(CO)}_4 + \text{PPh}_3 \xrightarrow{h\nu} [\text{Ni(CO)}_3(\text{PPh}_3)] + \text{CO}$$
  
(a) concentration of both the reactants                      (b) concentration of  $\text{Ni(CO)}_4$  only  
(c) Concentration of  $\text{PPh}_3$  only                      (d) The steric bulk of  $\text{PPh}_3$
- If the rate constants for different entering ligands are significantly different, it suggests that increasing the coordination number is important in the rate-determining step.  
What can you say about the mechanism it follow?  
(i) A                      (ii) D                      (iii)  $\text{I}_d$                       (iv)  $\text{I}_a$   
(a) Only (i)                      (b) (ii) & (iii)                      (c) only (ii)                      (d) (i) & (iv)
- Which of the following modification increase the rate of a square – planar complex?  
(a) Changing a trans ligand from  $\text{H}^-$  to  $\text{Cl}^-$                       (b) Changing the leaving group from  $\text{Cl}^-$  to  $\text{I}^-$   
(c) adding a bulky substituent to a cis ligand                      (d) increasing the positive charge on the complex
- The reaction of  $\text{cis-[PtMe}_2(\text{Me}_2\text{SO})(\text{PPh}_3)]$  with Py leads to  $\text{cis-[PtMe}_2(\text{Py})(\text{PPh}_3)]$  and the rate of reaction show no dependence on the concentration of Pyridine.  
What can you say about  $\Delta S^\ddagger$  value  
(a) will be positive                      (b) will be negative  
(c) may be positive or negative                      (d) Insufficient data

6. Which statement about the trans-effect and the trans-influence is correct?
- The trans-influence is a ground-state effect, whereas the trans-effect has a kinetic origin
  - The trans-effect is a ground-state effect, whereas the trans-influence has a kinetic origin
  - Both the trans-effect and trans-influence are ground-state effects
  - Rates of substitution are affected by the trans-effect but have nothing to do with the trans-influence of ligands
7. In the following reaction compound B is
- $$[\text{PtCl}_4]^{2-} + \text{NO}_2^- \longrightarrow \text{A} \xrightarrow{\text{NH}_3} \text{B}$$
- trans-[PtCl<sub>2</sub>(NO<sub>2</sub>)(NH<sub>3</sub>)]<sup>-</sup>
  - cis-[PtCl<sub>2</sub>(NO<sub>2</sub>)(NH<sub>3</sub>)]<sup>-</sup>
  - trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]
  - cis-[PtCl<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>2-</sup>
8. The reactions of [PtCl<sub>4</sub>]<sup>2-</sup> with NH<sub>3</sub> (reaction I) and of [PtCl<sub>4</sub>]<sup>2-</sup> with [NO<sub>2</sub>]<sup>-</sup> followed by NH<sub>3</sub> (reaction II) are:
- I: trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]; II: trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)(NO<sub>2</sub>)]<sup>-</sup>
  - I: cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]; II: trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)(NO<sub>2</sub>)]<sup>-</sup>
  - I: cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]; II: cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)(NO<sub>2</sub>)]<sup>-</sup>
  - I: trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]; II: cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)(NO<sub>2</sub>)]<sup>-</sup>
9. The platinum complex of NH<sub>3</sub> and Cl<sup>-</sup> ligands is an anti-tumor agent. The correct isomeric formula of the complex and its precursor are
- cis-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [PtCl<sub>4</sub>]<sup>-2</sup>
  - trans-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [PtCl<sub>4</sub>]<sup>-2</sup>
  - cis-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>+2</sup>
  - trans-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>+2</sup>
10. The reaction of [PtCl<sub>4</sub>]<sup>2-</sup> with NH<sub>3</sub>, gives rise to
- [PtCl<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>2-</sup>
  - trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]
  - [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]
  - cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]
11. The sequence of reactions, beginning with [PtCl<sub>4</sub>]<sup>2-</sup>, that will result in platinum (II) complex with four different ligands, Py, NH<sub>3</sub>, NO<sub>2</sub><sup>-</sup> and CH<sub>3</sub>NH<sub>2</sub> with two different set of ligands
- NH<sub>3</sub>, Py, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>NH<sub>2</sub>
  - Py, CH<sub>3</sub>NH<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, NH<sub>3</sub>
  - NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, Py, NO<sub>2</sub><sup>-</sup>
  - Py, NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, NO<sub>2</sub><sup>-</sup>



- (a) (i) & (ii)                      (b) (i) & (iii)                      (c) (ii) & (iii)                      (d) (ii) & (iv)

12. The reaction of  $[\text{Pt}(\text{PR}_3)_4]^{2+}$  with  $\text{Cl}^-$ , give rise to

- (a)  $[\text{Pt}(\text{PR}_3)_4\text{Cl}_2]$     (b) trans  $[\text{Pt}(\text{PR}_3)_2\text{Cl}_2]$   
 (c)  $[\text{PtCl}_4(\text{PR}_3)_2]^{2-}$     (d) cis  $[\text{Pt}(\text{PR}_3)_2\text{Cl}_2]$

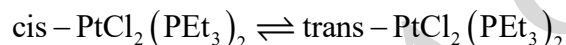
13. The reaction of  $[\text{Pt}(\text{NO}_2)\text{Cl}_3]^{2-}$  with ammonia to form:-

- (a) cis  $[\text{Pt}(\text{NO}_2)\text{NH}_3\text{Cl}_2]$     (b) trans  $[\text{Pt}(\text{NO}_2)(\text{NH}_3)\text{Cl}_2]$   
 (c)  $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{-1}$     (d)  $[\text{Pt}(\text{NO}_2)\text{Cl}_2(\text{NH}_3)_3]$

14. The reaction of  $[\text{PtCl}_4]^{2-}$  with two moles of  $\text{PPh}_3$  gives the product.

- (a) cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$     (b) trans- $[\text{PtCl}_2(\text{PPh}_3)_2]$   
 (c) Both (a) and (b)    (d)  $[\text{PtCl}_3(\text{PPh}_3)]$

15. cis- $\text{PtCl}_2(\text{PEt}_3)_2$  is stable in benzene solution at 25 °C. However, Small amounts of free triethylphosphine catalyze establishment of an equilibrium with trans isomer:



Which of the following isomer is more stable:

- (a) cis- $\text{PtCl}_2(\text{PEt}_3)_2$   
 (b) trans- $\text{PtCl}_2(\text{PEt}_3)_2$   
 (c) Both are equally stable  
 (d) can-not be determined

16. When the two isomers of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  react with Thiourea  $[\text{tu}=\text{S}=\text{C}(\text{NH}_3)_2]$ , one product is  $[\text{Pt}(\text{tu})_4]^{2+}$  and the other is  $[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}$ . Their initial isomers are:

- (a) cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and trans  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  respectively  
 (b) trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  respectively  
 (c) cis- $[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}$  and trans  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  respectively  
 (d) trans- $[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}$  and trans  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  respectively

17. How can one obtain the nucleophilic discrimination factor S (i.e. measure of the responsiveness of a square planar complex to the nucleophilicity) for the entering group?
- by calculating the  $R^2$  of the  $\log k_2(Y)$  versus the  $n_{pt}(Y)$  line
  - by calculating the Y-axis intercept of the  $\log k_2(Y)$  versus the  $n_{pt}(Y)$  line
  - by calculating the slope of  $\log k_2(Y)$  versus the  $n_{pt}$  line
  - None of these

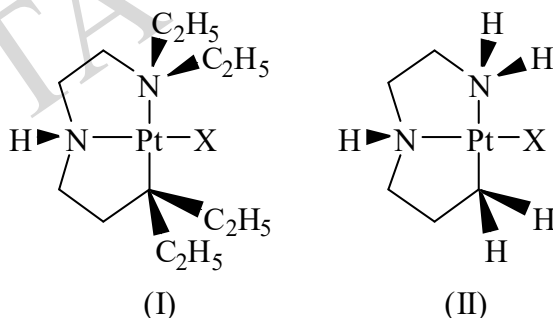
18. For the following reactions.



The compound Both 'A' and 'B' are white, diamagnetic crystalline compounds that given elemental analysis for empirical formula  $PtCl_2(NH_3)_2$ . However, A is most soluble in polar solvents, such as ethanol, while B is soluble in polar solvents, such as ethanol, while B is soluble in petroleum ether and  $CCl_4$ .

The correct statement are:

- A is cis platin
  - A is trans platin
  - B is trans platin
  - B is cis platin
19. Two Pt(II) complexes I and II as shown in figure below are attacked by  $Cl^-$  following associative mechanism.



On the basis of above information which of the following statements are true

- Rate of reaction is greater in case I
- Rate of reaction is greater in case II
- Rate is independent of ligand
- Rate is dependent on ligand.

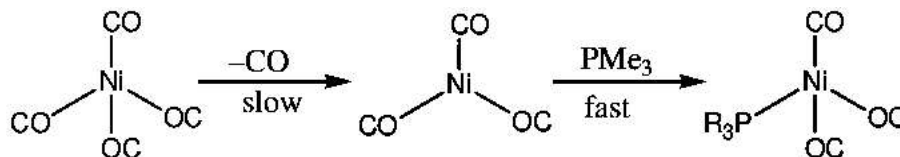
## ANSWER KEY

- |         |         |         |           |           |         |         |
|---------|---------|---------|-----------|-----------|---------|---------|
| 1. (b)  | 2. (b)  | 3. (d)  | 4. (d)    | 5. (a)    | 6. (a)  | 7. (a)  |
| 8. (b)  | 9. (a)  | 10. (d) | 11. (a)   | 12. (b)   | 13. (b) | 14. (a) |
| 15. (a) | 16. (a) | 17. (c) | 18. (a,c) | 19. (a,d) |         |         |

## HINTS & SOLUTION

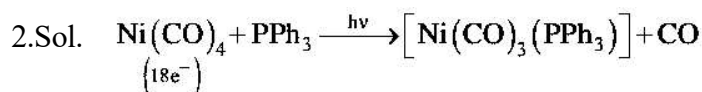
- 1.Sol.  $\text{Ni}(\text{CO})_4$  [L =  $\text{PMe}_3$ ,  $\text{P}(\text{OMe})_3$ ]  
 $\text{Ni}(\text{CO})_4$  Total valence electron around  
 $\text{Ni} = 10 + 4 \times 2 = 18$  electron

Substitution reaction at coordinatively saturated tetrahedral complexes with a 18 electron count like  $\text{Ni}(\text{CO})_4$  or  $\text{Ni}(\text{CO})_2(\text{PR}_3)_2$  follows a simple first order kinetics.

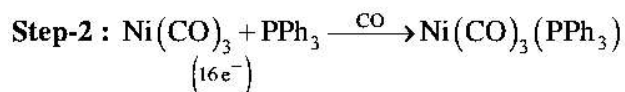
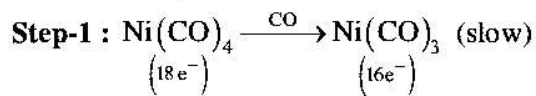


Since rate does not depend upon the concentration and nature of the ligand suggesting a dissociative mechanism.

**Correct answer is (b).**



Since  $\text{Ni}(\text{CO})_4$  follows 18 electron rule. So, it follow substitution via dissociation mechanism i.e.



So, the rate of reaction depends upon the concentration of  $\text{Ni}(\text{CO})_4$  only because this step is slowest step.

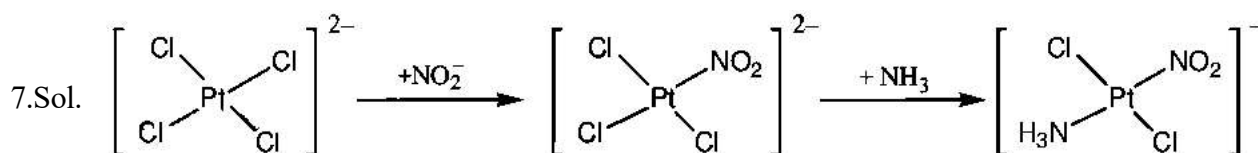
**Correct answer is (b)**

3.Sol. As the rate of reaction varies with  $\text{Nu}^\ominus$  (entering group) so, rate must dependent on concentration of entering group. It happens in  $\text{A}$  and  $\text{I}_a$  mechanism.

4.Sol. In square planar complex if we increase the positive charge then the rate of attack of  $\text{Nu}^-$  will increase as square planar complex undergo substitution by associative mechanism.

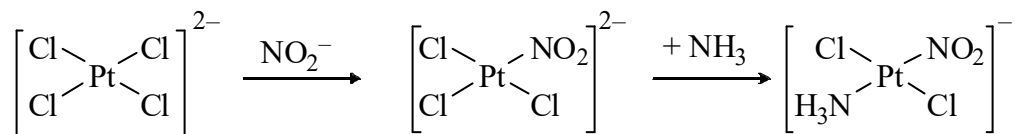
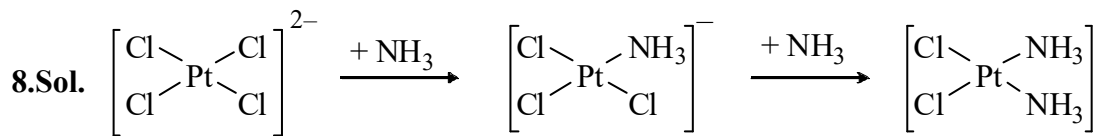
5.Sol. As the rate of reaction show no dependence on the concentration of pyridine so, it follow dissociative mechanism. Dissociative mechanism generally result in positive value of  $\Delta S^\ddagger$  because one species splits into two and entropy increases.

6.Sol. Trans-influence is ground state effect, whereas trans-effect is transition state effect.

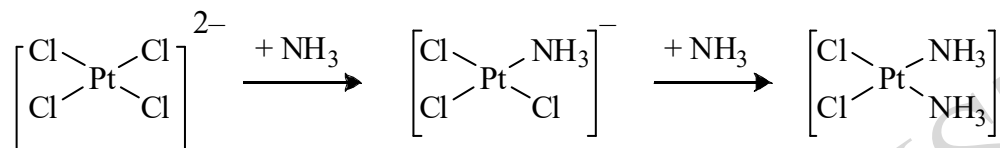


Trans effect  $\text{NO}_2^- > \text{Cl}^- > \text{NH}_3$

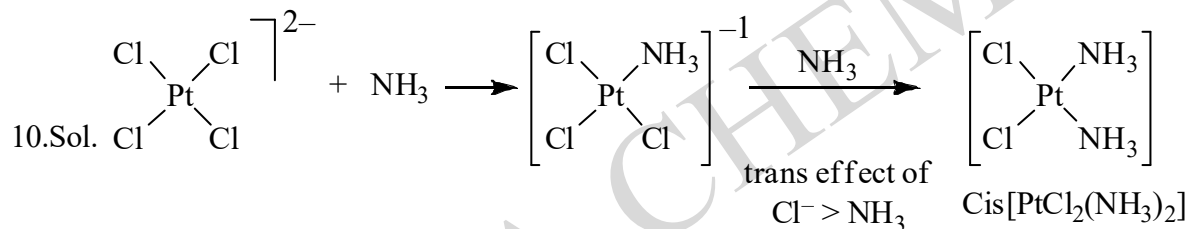
**Correct answer is (a)**



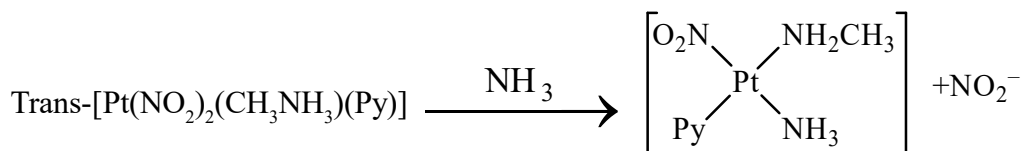
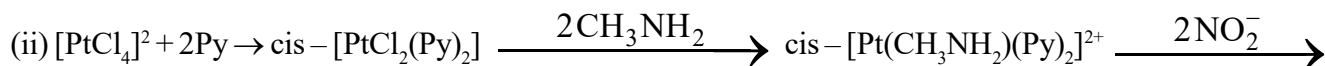
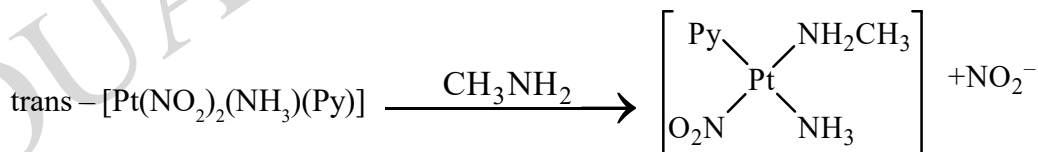
9.Sol. Trans effect of  $\text{Cl}^- > \text{NH}_3$  Anti-tumour agent is cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

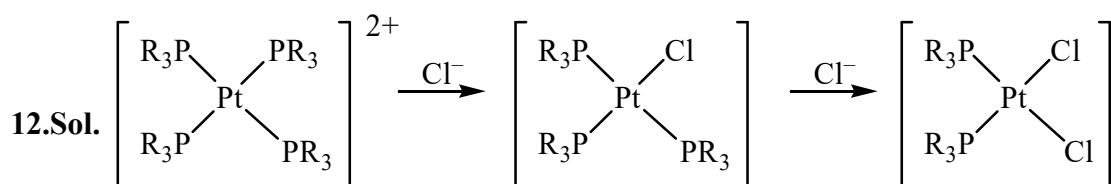


Correct answer is (a)

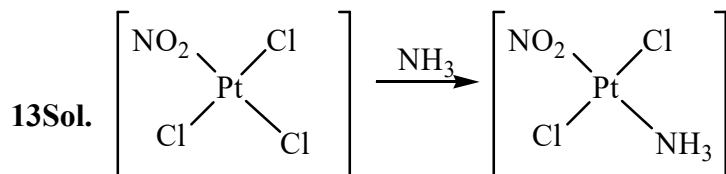


Correct option is (d)





As trans effect of  $\text{PR}_3$  is greater than  $\text{Cl}^-$



trans effect of  $\text{NO}_2$  is greater than  $\text{Cl}^-$  so, trans  $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]$

14.Sol. It is due to cis influence effect which can be defined as ability of a ligand A to weaken a bond between metal and ligand B, which is cis to A.

15.Sol. The cis isomer has the higher bond energy (actually, the lower overall energy and collectively stronger bonding), since rearrangement to the trans isomer is endothermic.

16.Sol. Both chloride of cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  are initially replaced. The tu's are then trans to the  $\text{NH}_3$  which are replaced because of the strong trans effect of tu, resulting in  $[\text{Pt}(\text{tu})_4]^{2+}$ .

Trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  reacts with thiourea (tu) to form trans- $[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}$ ; the first  $\text{Cl}^-$  is displaced and the strong trans effect of tu leads to preferential replacement of second  $\text{Cl}^-$ .

17.Sol. Since  $\log k_2(Y) = S n_{\text{Pt}}(Y) + C$ , S equals to the slope of line, the slope of the  $\log k_2(Y)$  versus the  $n_{\text{Pt}}(Y)$  line provides S that is measure of the responsiveness of a square-planar complex to the nucleophilicity of the entering group (also called nucleophilic discrimination factor).

18.Sol. (i) A is cis platin as it is soluble in polar solvent such as ethanol.

B is trans transplatin as it is soluble in non-polar solvent such as petroleum ether and  $\text{CCl}_4$ .

19.Sol. The ethyl substituted complex presents a greater degree of steric hindrance to an incoming  $\text{Cl}^-$  ion nucleophile. Since the rate-determining step for associative substitution of  $\text{X}^-$  by  $\text{Cl}^-$  is the formation of a Pt-Cl bond, the more hindered complex will react more slowly.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

## DPP- (25)

- A reaction sequence in which an intermediate of reduced coordination number is formed by the departure of the leaving group is called:  
(a) An associative mechanism (b) A dissociative mechanism  
(c) An interchange associative mechanism (d) None of these
- The rate-determining step in octahedral complex substitution is believed to be:  
(a) an associative step (b) a dissociative step  
(c) an interchange step (d) any of these
- The reaction  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-} + \text{X}^- \rightarrow [\text{Co}(\text{CN})_5\text{X}]^{2-} + \text{H}_2\text{O}$  follows a/an:  
(a) Interchange dissociative ( $I_d$ ) mechanism  
(b) Dissociative (D) mechanism  
(c) Associative (A) mechanism  
(d) Interchange Associative ( $I_a$ ) mechanism
- The order for rate of dissociation of CO cis to the ligands (CO,  $\text{PPh}_3$ , I $^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ) for the given complexes  $[\text{Cr}(\text{CO})_5\text{Cl}]^-$ ,  $[\text{Cr}(\text{CO})_5\text{Br}]^-$ ,  $[\text{Cr}(\text{CO})_5\text{I}]^-$ ,  $[\text{Cr}(\text{CO})_6]$ ,  $[\text{Cr}(\text{CO})_5(\text{PPh}_3)]$  follow the order  
(a)  $[\text{Cr}(\text{CO})_6] < [\text{Cr}(\text{CO})_5(\text{PPh}_3)] < [\text{Cr}(\text{CO})_5\text{I}]^- < [\text{Cr}(\text{CO})_5\text{Br}]^- < [\text{Cr}(\text{CO})_5\text{Cl}]^-$   
(b)  $[\text{Cr}(\text{CO})_5(\text{PPh}_3)] < [\text{Cr}(\text{CO})_6] < [\text{Cr}(\text{CO})_5\text{I}]^- < [\text{Cr}(\text{CO})_5\text{Br}]^- < [\text{Cr}(\text{CO})_5\text{Cl}]^-$   
(c)  $[\text{Cr}(\text{CO})_5\text{I}]^- < [\text{Cr}(\text{CO})_5\text{Br}]^- < [\text{Cr}(\text{CO})_5\text{Cl}]^- < [\text{Cr}(\text{CO})_6] < [\text{Cr}(\text{CO})_5(\text{PPh}_3)]$   
(d)  $[\text{Cr}(\text{CO})_5\text{I}]^- < [\text{Cr}(\text{CO})_5\text{Br}]^- < [\text{Cr}(\text{CO})_5\text{Cl}]^- < [\text{Cr}(\text{CO})_5(\text{PPh}_3)] < [\text{Cr}(\text{CO})_6]$
- The reaction of  $[\text{Ru}(\text{CO})_3(\text{PR}_3)(\text{SiCl}_3)_2]$  with Y to give  $[\text{Ru}(\text{CO})_2\text{Y}(\text{PR}_3)(\text{SiCl}_3)_2]$  undergoes by dissociative mechanism. What will be the mechanism if ligand Y is replaced by another ligand having different  $\text{pK}_a$  value but similar

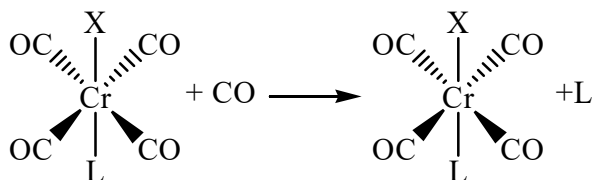
cone. angle.

- (a) It will remain dissociative (b) It will be associative  
(c) It can be asosciative or dissociative (d) Insufficient data

6. The rate constant for the formation of  $[\text{CoX}(\text{NH}_3)_5]^{2+}$  from  $[\text{Co}(\text{NH}_3)_6]^{2+}$  where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{N}_3^-$  and  $\text{SCN}^-$  differ by no more than a factor of 2. The mechanism of this substitution is

- (a) D (b) A (c)  $\text{I}_a$  (d)  $\text{I}_d$

7. The reaction



Occurs by a dissociative mechanism and the first order rate constant  $k_1$  vary with the nature of substituent X follows the order:

- (a)  $\text{CO} < \text{P}(\text{OPh})_3 < \text{P}(\text{nBu})_3$  (b)  $\text{P}(\text{nBu})_3 > \text{P}(\text{OPh})_3 > \text{CO}$   
(c)  $\text{CO} < \text{P}(\text{OPh})_3 \approx \text{P}(\text{nBu})_3$  (d)  $\text{P}(\text{nBu})_3 \approx \text{P}(\text{OPh})_3 > \text{CO}$

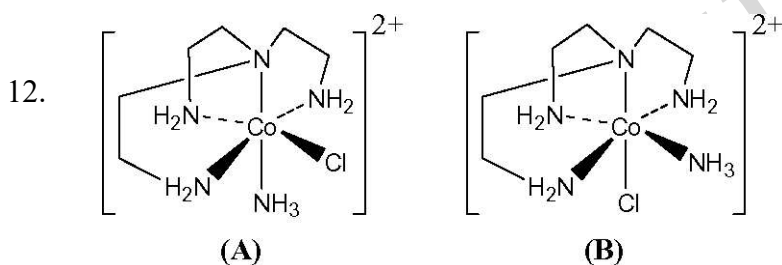
8. Find the correct statements:

- (a) Octahedral substitution reaction that go through a square pyramidal intermediate result in the retention of the original geometry. A trigonal bipyramidal intermediate may lead to isomerization.  
(b) Octahedral substitution reactions that go through a square-pyramidal intermediate do not retain the original geometry. A trigonal bipyramidal intermediate may lead to isomerization.  
(c) Octahedral substitution reactions that go through a trigonal bipyramidal intermediate result in retention of the original geometry. A square pyramidal intermediate may lead to isomerization.  
(d) Isomerism is not observed octahedral complexes.

9. For  $\text{OH}^-$  catalysed  $\text{S}_\text{N}1$  conjugate base mechanism of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ , the species obtained in the first step of the reaction is/are

- (a)  $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+} + \text{Cl}^-$  (b)  $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+ + \text{H}_2\text{O}$   
(c)  $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)]^{2+} + \text{Cl}^-$  (d)  $[\text{Co}(\text{NH}_3)_5\text{Cl}(\text{OH})]^+$  only

10. A true statement about base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
- It is a first order reaction
  - The rate determining step involves the dissociation of chloride in  $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$
  - The rate is independent of the concentration of the base
  - The rate determining step involves the abstraction of a proton from  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
11. The correct statement about base hydrolysis of  $[\text{Co}(\text{py})_4\text{Cl}_2]^+$  (py = pyridine) is
- rate expression is,  $\text{Rate} = k [\text{Co}(\text{py})_4\text{Cl}_2]^+ [\text{OH}^-]$
  - reaction does not depend on hydroxide ion concentration
  - reaction proceeds through  $\text{S}_{\text{N}}1\text{CB}$  mechanism
  - intermediate involved in this reaction is  $[\text{Co}(\text{py})_4\text{Cl}_2(\text{OH})]$



The isomers A and B undergo base hydrolysis by forming a trigonal bipyramidal intermediate. The correct statement is

- A reacts faster than B and both results in a mixture of products
  - B reacts faster than A and both results in a mixture of products
  - A reacts faster than B and B result in a mixture of products.
  - B reacts faster than A and A result in a mixture of products.
13. In the hydrolysis of  $\text{trans}-[\text{Co}(\text{en})_2\text{Cl}(\text{A})]^+$ , if the leaving group is chloride, the formation of cis product is the least, when A is,
- $\text{NO}_2^-$
  - $\text{NCS}^-$
  - $\text{Cl}^-$
  - $\text{OH}^-$
14. Hydrolysis of  $\text{trans}-[\text{CoLCl}(\text{en})_2]^+$  ( $\text{L} = \text{NO}_2^-, \text{NCS}^-, \text{OH}^-, \text{Cl}^-$ ) results in a product (A). The tendency to form cis-isomer of the product (A) follows the order



- (a)  $L = \text{NO}_2^- < \text{NCS}^- < \text{OH}^- < \text{Cl}^-$       (b)  $L = \text{NO}_2^- < \text{Cl}^- < \text{NCS}^- < \text{OH}^-$
- (c)  $L = \text{OH}^- < \text{Cl}^- < \text{NO}_2^- < \text{NCS}^-$       (d)  $L = \text{OH}^- < \text{NCS}^- < \text{Cl}^- < \text{NO}_2^-$
15. What is the effect of temperature on stereochemistry of product in the substitution of ammonia for both chlorides in  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ .
- (a) Below  $-33^\circ\text{C}$  ammonia inversion of configuration is observed
- (b) Above  $25^\circ\text{C}$  in ammonia inversion of configuration is observed.
- (c) Stereochemistry is independent of temperature
- (d) Above  $25^\circ\text{C}$  ammonia product is unstable.
16. Which of the following statements are correct for  $[\text{Ni}(\text{en})_3]^{2+}$  complex
- (i) It can undergo isomerisation
- (ii) It does not show any isomerised product
- (iii) Isomerisation is observed by an intramolecular twist
- (iv) Isomerisation is observed by breaking of bond.
- (a) (i) and (iii)      (b) (i) and (iv)      (c) only (ii)      (d) only (i)
17. Which of the following will decrease the rate of reaction for dissociatively activated  $\text{Rh(III)}$  complex.
- (a) An increase in overall charge on the complex
- (b) Changing the leaving group from  $\text{NO}_3^-$  to  $\text{Cl}^-$
- (c) Changing the leaving group from  $\text{Cl}^-$  to  $\text{I}^-$
- (d) Changing the cis ligands from  $\text{NH}_3$  to  $\text{H}_2\text{O}$

### ANSWER KEY

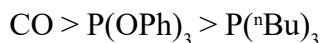
- |     |     |     |     |     |         |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (b) | 2.  | (b) | 3.  | (a)     | 4.  | (a) | 5.  | (a) | 6.  | (d) | 7.  | (a) |
| 8.  | (a) | 9.  | (b) | 10. | (b)     | 11. | (b) | 12. | (c) | 13. | (a) | 14. | (b) |
| 15. | (a) | 16. | (a) | 17. | (a,b,d) |     |     |     |     |     |     |     |     |

## HINTS & SOLUTION

- 1.Sol.** In dissociative mechanism an intermediate with reduced coordination number is formed.
- 2.Sol.** The rate-determining step in octahedral complex substitution is believed to be dissociative step.
- 3.Sol.** Correct option is (a)
- 4.Sol.** Two factors need to be considered:
- (i) The best  $\pi$  acceptors ( $\text{CO}$ ,  $\text{PPh}_3$ ) slow the dissociation of  $\text{CO}$  in the cis position;  $\pi$  donors (halides) speed the dissociation.
- (ii) Halides are weaker  $\pi$  donors relative to phosphines and carbon monoxide. As a result there is less electron density for  $\pi$  back bonding with halides and weaker  $\text{M} - \text{CO}$  bond in complex. the  $\pi$  donor ability help in stabilizing the square pyramidal transition state.
- 5.Sol.** If cone angle is nearly same then there will be no change in mechanism. It will remain dissociative.
- 6.Sol.** It will undergo reaction by  $I_d$  mechanism. No intermediate is formed and bond breaking is important than bond formation.
- 7.Sol.** Rate of reaction for dissociative mechanism

$$\propto \frac{1}{\pi \text{ acceptor tendency of trans ligand}}$$

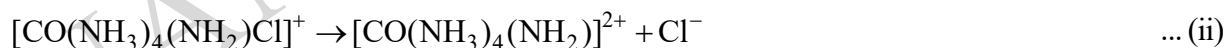
order of  $\pi$  acceptor tendency is



So, the first order rate constant varies

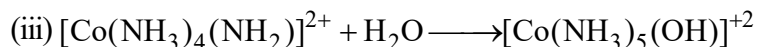
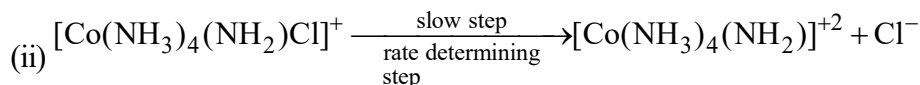
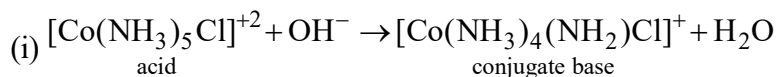


- 8.Sol.** Isomerization is possible in octahedral complexes when trigonal bipyramidal intermediate is formed.



Correct option is (b)

- 10.Sol.** Substitution nucleophilic unimolecular conjugate base mechanism.

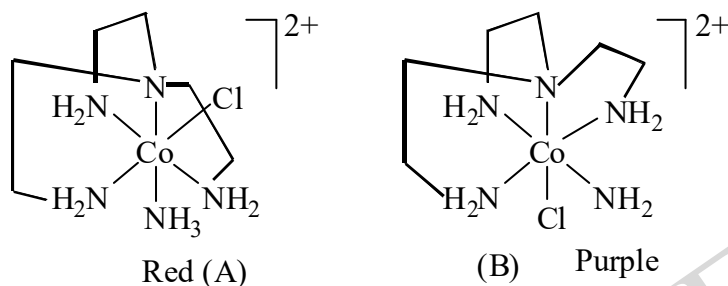


Correct answer is (b)

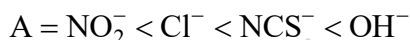
11.Sol. The base hydrolysis of  $[\text{Co}(\text{Py})_4\text{Cl}_2]^+$ , does not depend on hydroxide ion concentration because here pyridine having no acidic hydrogen and  $\text{OH}^-$  ion does not abstract any proton in this case and conjugate base not formed.

Correct option is (b)

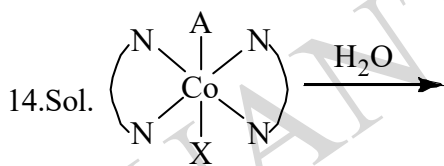
12.Sol. The  $[\text{Co}(\text{tren})(\text{NH}_3)\text{Cl}]^{2+}$  ion exists in two isomeric forms having the red and the purple colours. In the red isomer, the leaving group  $\text{Cl}^-$  is trans to the  $-\text{NH}_2$  group and in purple isomer the leaving group (Halogen) is trans to the amino group which have no proton. The red Isomer of  $[\text{Co}(\text{tren})(\text{NH}_3)\text{Cl}]^{2+}$  ion is hydrolyzed much more faster than the purple isomer



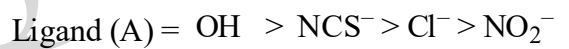
13.Sol. The  $\pi$ -donor ligands such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , N-bonded NCS etc stabilize the TBP intermediate and favour the stereochemical change. The trans-forms tendency to isomers in the order



Correct option is (a)



Extent of cis isomer in the product  $\propto$  II donor tendency of trans ligand (A)



X. cis  
Content

Correct option is (b)

15.Sol. At low temperature ( $-33^\circ\text{C}$ ) or below in liquid ammonia there is inversion of configuration; at higher temperature (above  $25^\circ\text{C}$ ) in liquid ammonia, alcohol solution, or solid exposed to gaseous ammonia there is retention.

16.Sol.  $[\text{Ni}(\text{en})_3]^{2+}$  undergo isomerization by an intramolecular twist following two possible path the baird twist and the Ray-Dutt twist.

**Sol.** Since the leaving group is invariably negatively charged, increasing the positive charge on complex will retard the rate of  $M-X$  bond. For a dissociatively activated reaction, this change will result in a decreased rate.

Change of leaving group from nitrate to chloride results in a decreased rate. The explanation offered is that  $Co-Cl$  bond is stronger than the  $Co-ONO_2$  bond. For a dissociatively activated reaction, a stronger bond to the leaving group will result in a decreased rate.

This change will have little or no effect on the rate. For a dissociatively activated reaction, the bond between the entering group and the metal is formed subsequent to the rate-determining step.

These two ligands differ in their  $\sigma$  basicity. The less basic ligand,  $H_2O$  will decrease the electron density at the metal and will destabilize the coordinatively unsaturated activated complex. Therefore, this change from  $NH_3$  to less basic ligand  $H_2O$  will result in a decreased rate.



# QUANTA CHEMISTRY

An Institute of Chemical Sciences

CSIR-NET | IIT-GATE | IIT-JAM | Other MSc. Entrance

---

## DPP- (26)

---

1. Inner sphere and outer sphere redox mechanism are different in that:
  - (a) The inner-sphere mechanism involves simple electron transfers, while the outer-sphere mechanism involves atom transfers. The inner-sphere mechanism forms a bridged transition state involving the reactant coordination spheres.
  - (b) The inner-sphere mechanism involves atom transfers, while the outer-sphere mechanism involves simple electron transfers. The outer sphere mechanism forms a bridged transition state involving the reactant coordination spheres, while the inner-sphere one does not.
  - (c) The inner-sphere mechanism involves atom transfers, while the outer-sphere mechanism involves simple electron transfer. The inner sphere mechanism form a bridged transition state involving the reactants coordination spheres, while the outer-sphere one does not
  - (d) None of these
2. Usually, photosubstitution and photoisomerism are associated with:
  - (a) exclusively photooxidation reaction
  - (b) d-d transition only
  - (c) d-d- transitions and photooxidation reactions with charge transfer transitions
  - (d) charge transfer transitions only
3. Self- exchange electron transfer is fastest in
  - (a)  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$
  - (b)  $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$
  - (c)  $[\text{Cr}(\text{OH}_2)_6]^{2+/3+}$
  - (d)  $[\text{Fe}(\text{OH}_2)_6]^{2+/3+}$
4. The mechanism of the reaction between  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{bpy})_3]^{3+}$  (bpy = 2,2'-bipyridine) is

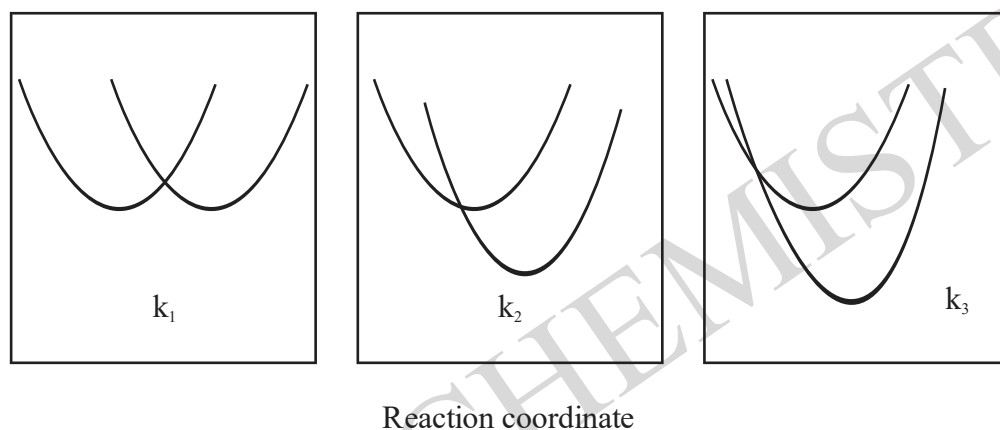
(a) outer-sphere electron-transfer

(b) inner-sphere electron-transfer

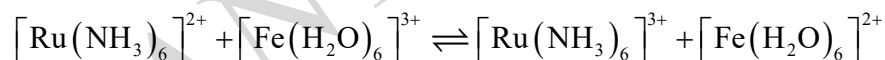
(c) self-exchange reaction

(d) ligand exchange followed by electron-transfer

5. The potential energy (PE) versus reaction coordinate diagrams for electron transfer reactions with rate constants  $k_1$ ,  $k_2$  and  $k_3$ , are given below. The increasing order of the rate constants is

(a)  $k_2 < k_3 < k_1$ (b)  $k_2 < k_1 < k_3$ (c)  $k_3 < k_2 < k_1$ (d)  $k_3 < k_1 < k_2$ 

6. In the following redox reaction with an equilibrium constant  $K = 2.0 \times 10^8$ ,

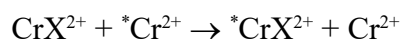


the self exchange rates for oxidant and reductant are  $5.0 \text{ M}^{-1} \text{ s}^{-1}$  and  $4.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  respectively.

The approximate rate constant ( $\text{M}^{-1} \text{ s}^{-1}$ ) for the reaction is

(a)  $3.16 \times 10^6$ (b)  $2.0 \times 10^6$ (c)  $6.32 \times 10^6$ (d)  $3.16 \times 10^4$ 

7. For the following reaction



where  ${}^*\text{Cr}$  is radioactive  ${}^{51}\text{Cr}$

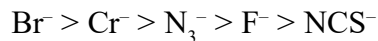


Which of the following statement are true.

(i) Reaction proceed by inner sphere mechanism

(ii) Reaction proceed by outer sphere mechanism

(iii) The order of rate constant for the probable mechanism is



- (a) (i) & (iii)                      (b) (i) & (iv)                      (c) (ii) & (iii)                      (d) (ii) & (iv)

8. In the reaction of azido pentaammine cobalt (III) ion with  $\text{V}^{2+}(\text{aq})$  the product  $[\text{V}(\text{OH}_2)_6]^{3+}$  detected. The mechanism of the reaction is

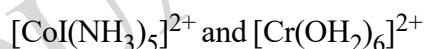
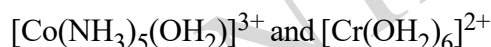
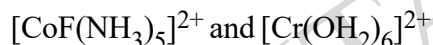
- (a) Interchange dissociative                      (b) Interchange associative  
(c) Inner sphere electron transfer                      (d) Outer sphere electron transfer

9. The intermediate  $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$  is detected in the reaction of  $[\text{Co}(\text{NCS})(\text{NH}_3)_5]^{2+}$  with  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  in aqueous medium to produce  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

The mechanism of the reaction is

- (a) Interchange dissociative                      (b) Interchange associative  
(c) Inner sphere electron transfer                      (d) Outer sphere electron transfer

10. Consider the following pairs of complexes



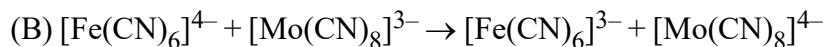
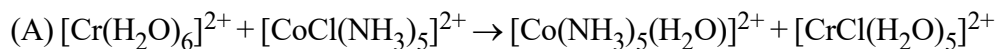
The electron transfer rate will be fastest in the pair

- (a)  $[\text{CoF}(\text{NH}_3)_5]^{2+}$  and  $[\text{Cr}(\text{OH}_2)_6]^{2+}$                       (b)  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$  and  $[\text{Cr}(\text{OH}_2)_6]^{2+}$   
(c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Cr}(\text{OH}_2)_6]^{2+}$                       (d)  $[\text{CoI}(\text{NH}_3)_5]^{2+}$  and  $[\text{Cr}(\text{OH}_2)_6]^{2+}$

11. Second-order are constant for the reaction between  $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$  ( $n = 3$  for  $\text{X} = \text{NH}_3$  and  $\text{H}_2\text{O}$ ;  $n = 2$  for  $\text{X} = \text{Cl}^-$ ) and  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  at room temperature varies with the X as

- (a)  $\text{NH}_3 > \text{H}_2\text{O} > \text{H}_2\text{O}$                       (b)  $\text{Cl}^- > \text{H}_2\text{O} > \text{NH}_3$   
(c)  $\text{NH}_3 > \text{Cl}^- > \text{H}_2\text{O}$                       (d)  $\text{H}_2\text{O} > \text{NH}_3 > \text{Cl}^-$

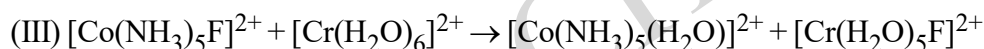
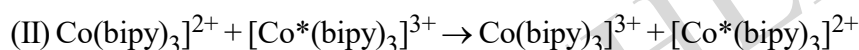
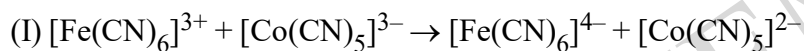
12. Consider the reactions



Which one of the following is the correct statement?

- (i) Both involve an inner sphere mechanism
  - (ii) Both involve an outer sphere mechanism
  - (iii) Reaction A follows inner sphere and reaction B follows outer sphere mechanism
  - (iv) Reaction A follows outer sphere and reaction B follows inner sphere mechanism
- (a) i                      (b) ii                      (c) iv                      (d) iii

13. Consider the statements A-D regarding equations I-III:



- (A) Marcus equation is applicable to I and II.
- (B) Marcus equation is applicable to II only
- (C) Equations I and II involve inner sphere electron transfer
- (D) Equations I and III involve inner sphere electron transfer.

The correct statements are

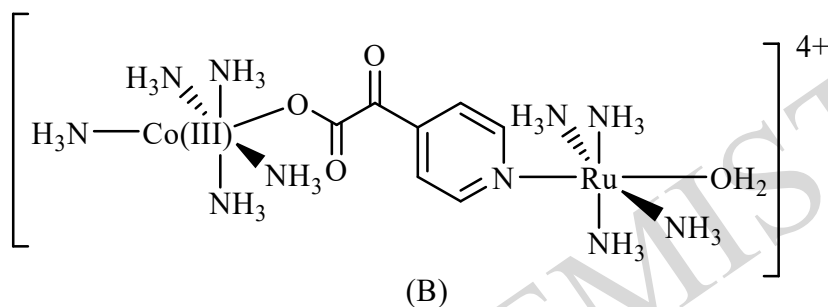
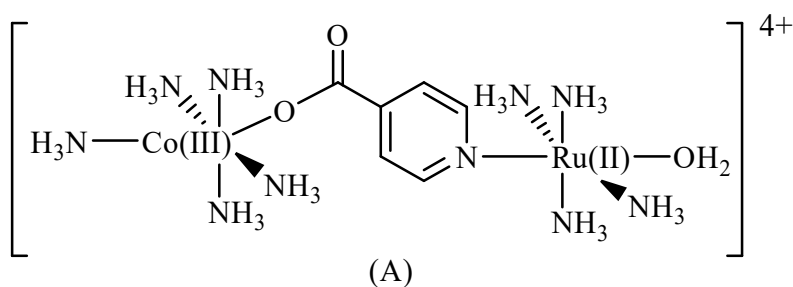
- (a) A and B                      (b) B and C                      (c) B and D                      (d) C and D

14. The oxidation of a metal centre by oxidoanions Mo(IV) by  $NO_3^-$  ions takes place by

- (a) Inner sphere mechanism                      (b) Outer sphere mechanism
- (c) Interchange dissociative                      (d) Interchange associative

15. The rate constant for the oxidation of Ru(II) by Co(III) centre in bimetallic complex (A) is  $1.0 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , whereas the rate constant for complex (B) is  $1.6 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .





Based upon these observations which of the following statements is true.

- (a) It follow outer sphere mechanism
- (b) Marcus equation is valid for complex A
- (c) Marcus equation is valid for complex B
- (d) It follow inner sphere mechanism.

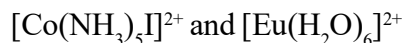
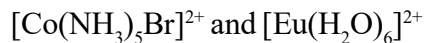
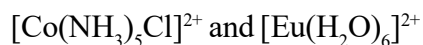
16. The reaction of  $\text{V}^{2+}(\text{aq})$  with  $\text{V}^{3+}(\text{aq})$  is facilitated by inner sphere mechanism under which of the following condition.

- (a) pH of aqueous solution should be slightly acidic
- (b) pH of aqueous solution should be slightly basic.
- (c) Independent of pH of solution
- (d) Insufficient data to predict

17. In inner sphere mechanism the products formed can be separated by

- (a) Column chromatography
- (b) ion-exchange techniques
- (c) fractional distillation
- (d) All of above

18. Consider the following pair of complexes :

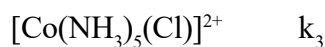
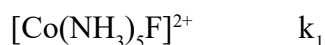


The electron transfer rate will be fastest in the pair

- (a)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  and  $[\text{Eu}(\text{H}_2\text{O})_6]^{2+}$       (b)  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$  and  $[\text{Eu}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$  and  $[\text{Eu}(\text{H}_2\text{O})_6]^{2+}$       (d) will be same for all

19. The rate constants for the reaction of  $[\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$  with  $[\text{Co}(\text{CN})_5]^{3-}$  is given as

Oxidant       $k(\text{M}^{-1} \text{S}^{-1})$



Which is the correct order of rate constant

- (a)  $k_1 > k_2 > k_3$       (b)  $k_1 = k_2 > k_3$       (c)  $k_3 > k_2 > k_1$       (d)  $k_3 > k_1 > k_2$

20. The relative values of rate constants for the following electron-transfer reactions in aqueous solution are given below.

Reaction	Reactants	$k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
I	$[\text{Ru}(\text{NH}_3)_6]^{3+} + [\text{Ru}(\text{NH}_3)_6]^{2+}$	$k_1$
II	$[\text{Co}(\text{NH}_3)_6]^{3+} + [\text{Ru}(\text{NH}_3)_6]^{2+}$	$k_2$
III	$[\text{Co}(\text{NH}_3)_6]^{3+} + [\text{Co}(\text{NH}_3)_6]^{2+}$	$k_3$

Which of the following statements are true on the basis of above information.

- (a) The rate of electron transfer is fastest in case I.  
 (b) For reaction II  $\Delta G^\circ = 0$   
 (c) For reaction I and III  $\Delta G^\circ = 0$   
 (d) Reaction I undergo by outer sphere mechanism

21. Which of the following statements are correct for electron-transfer process.

- (a) In inner sphere electron-transfer process, there is always electron and ligand transfer between reagents.
- (b) For self redox reaction  $\Delta G = 0$  in case of outer sphere mechanism.
- (c) Rate of electron transfer in case of inner sphere mechanism depends upon polarizability of bridging ligand.
- (d) Marcus – Hush equation is valid for inner sphere mechanism.

22. Which of the following statements is / are true?

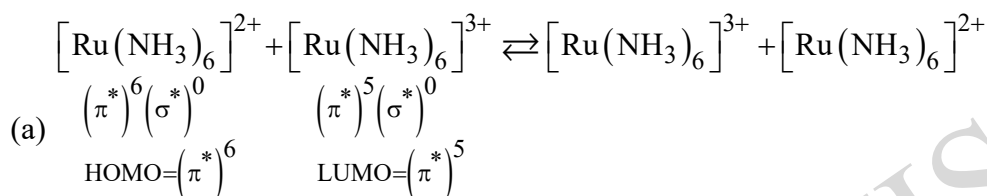
- (a) The high spin  $d^4$  complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  is labile, but the low-spin  $d^4$  complex ion  $[\text{Cr}(\text{CN})_6]^{4-}$  is inert.
- (b) Two separate water exchange rate are found for  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  in aqueous solution.
- (c) Exchange of an  $\text{H}_2\text{O}$  ligand on  $[(\text{CO})_3\text{Mn}(\text{H}_2\text{O})_3]^+$  is much more rapid than  $[(\text{CO})_3\text{Re}(\text{H}_2\text{O})_3]^+$ .
- (d) None of above

### ANSWER KEY

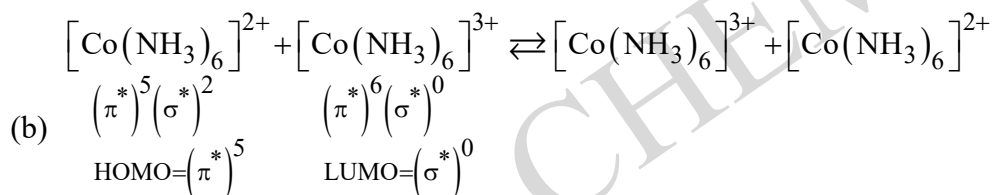
- |     |         |     |     |     |     |     |     |     |     |     |         |     |       |
|-----|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|---------|-----|-------|
| 1.  | (c)     | 2.  | (c) | 3.  | (a) | 4.  | (a) | 5.  | (d) | 6.  | (b)     | 7.  | (a)   |
| 8.  | (d)     | 9.  | (c) | 10. | (d) | 11. | (b) | 12. | (d) | 13. | (c)     | 14. | (a)   |
| 15. | (d)     | 16. | (b) | 17. | (b) | 18. | (a) | 19. | (c) | 20. | (a,c,d) | 21. | (b,c) |
| 22. | (a,b,c) |     |     |     |     |     |     |     |     |     |         |     |       |

## HINTS & SOLUTION

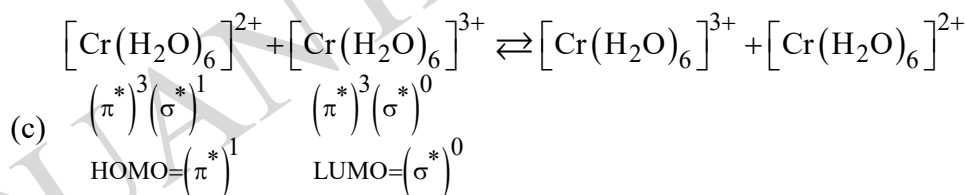
- 1Sol. In inner sphere mechanism bridged complex is formed and atom may also transfer. But this does not happen in outer sphere mechanism.
- 2Sol. usually, photosubstitution and photoisomerism are associated with d-d- transition and photoredox reactions with charge-transfer transitions.
- 3Sol. Electron transfer reactions by self-exchange electron transfer is fast when HOMO is  $\pi^*$  and LUMO is also  $\pi^*$  i.e. electron transfer is from  $\pi^*$  of reductant to the  $\pi^*$  of oxidant.



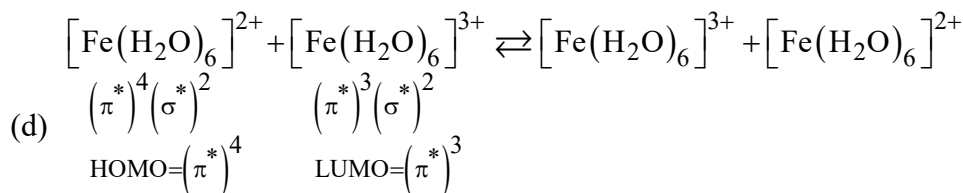
Reaction is fast



Reaction is slow



Reaction is slow



Reaction is fast

Both reactions (a) and (d) are fast but reaction (a) is much faster than (d) because there is small change in M-L bond length in reaction (a) i.e. less activation energy is required.

**Correct option is (a)**

- 4Sol. The mechanism of the reaction between  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{bpy})_3]^{3+}$  is outer sphere electron transfer.

Correct option is (a)

5Sol. (d) The order of increasing rate constant is

$$k_3 < k_1 < k_2$$

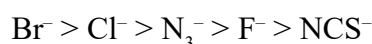
$k_1$  because of the symmetrical structure is more than  $k_3$ , value of which is least among the three.

6Sol.  $k_{12} = (k_{11} K k_{22} f)^{1/2} = (5 \times 4 \times 10^3 \times 2 \times 10^8 \times 1.0)^{1/2} = 20 \times 10^5 = 2.0 \times 10^6$

Correct option is (b)

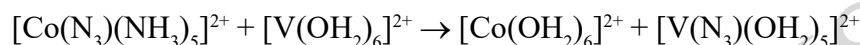
7Sol. The reaction proceed through inner sphere mechanism where X act as bridging ligand.

There order of rate is



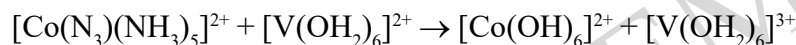
The order for rate is based upon HSAB principle & polarisability.

8Sol. If reaction proceed through inner sphere mechanism



The final product obtained is  $[\text{V}(\text{N}_3)(\text{OH}_2)_5]^{2+}$ , ligand is transferred.

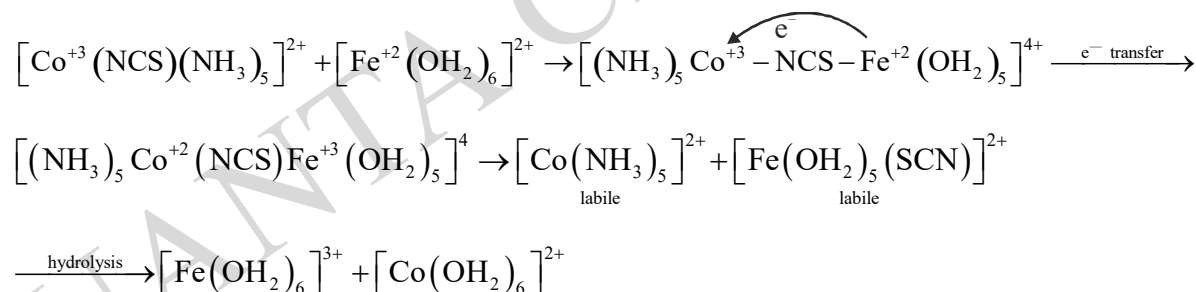
If reaction proceed through outer sphere mechanism



Here  $[\text{V}(\text{OH}_2)_6]^{3+}$  product is formed

So, reaction proceed through outer sphere mechanism.

9Sol. (c)



Final products

$r \times n$  goes via inner sphere mechanism.

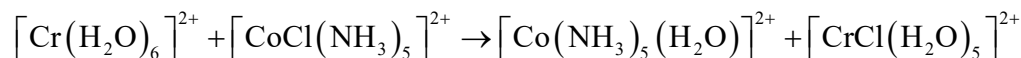
10Sol. In all the reactant one of the reactant is  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  which is very labile complex.

As the size of halide increase bridging tendency increases. Hence the rate of electron transfer also increases.

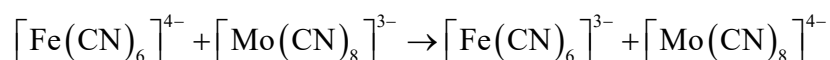
11Sol.  $\text{Cl}^- > \text{H}_2\text{O} > \text{NH}_3$

Correct option is (b)

12Sol. Reaction,



follows inner sphere mechanism because it involves exchange of ligand. While reaction,



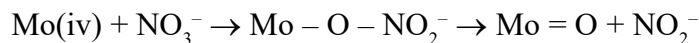
follows outer sphere mechanism because it involves only transfer of charge.

13Sol. In reaction (I) & (III) electron transfer take place by inner sphere mechanism but in reaction (II) electron transfer

take place by mechanism. Marcus equation is valid only in outer sphere mechanism.

Correct option is (c)

- 14Sol.** The oxidation of a metal centre by oxidoanions take place by inner – sphere process and is important in some enzymes. In oxidation of Mo(IV) by  $\text{NO}_3^-$  ions, an O atom of the nitrate ion binds to Mo atom, facilitating the electron transfer from Mo to N and then remains bound to Mo(VI) product.



- 15Sol.** In both complexes there is pyridine carboxylic acid group bridging the two metal centres. These groups are bound to both metal atoms and could facilitate an electron – transfer process through the bridge, suggest an inner-sphere mechanism. The difference in rate constant is due to change in substitution pattern of pyridine ring, confirms that the bridge must be playing role in the electron transfer.

Marcus equation is valid in case of outer sphere complex.

- 16Sol.**  $\text{V}^{2+}$  is  $d^3$  and likely to be inert,  $\text{V}^{3+}$  is  $d^2$  and labile. At low  $[\text{H}^+]$  (slightly basic condition), In equilibrium mixture of  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{V}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  may persist. The hydroxo ligand of  $[\text{V}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  may permit a bridging interaction with labile  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  to form  $[\text{V}(\text{H}_2\text{O})_5(\mu\text{-OH})\text{V}(\text{H}_2\text{O})_5]^{4+}$  to facilitate an inner sphere electron transfer mechanism.

- 17Sol.** During transfer of ligand in these reaction inert product if formed. So, the products can be separated by ion exchange techniques and their composition can be determined.

- 18Sol.** The order is reverse as generally expected for Halides in inner sphere mechanism. The explanation offered for these rate constants is that the thermodynamic stabilities of  $\text{EuX}^+$  species helps to drive the reaction faster for  $\text{Cl}^-$  with slower rates and stabilities as we go down the series.

- 19Sol.** The rate constant depends upon polarizability of the ligand.

Therefore correct order of rate constant is

$$k_3 > k_2 > k_1$$

The value of  $k_1 = 1.8 \times 10^3$

$$k_2 = 9.3 \times 10^4$$

$$k_3 = 5 \times 10^7$$

- 20. Sol.** I and III are self-exchanges and II is corresponding cross reaction. Therefore  $\Delta G^\circ = 0$  for I and III reaction. In case I,  $k_1$  is relatively large and indicates fast electron transfer. A second row metal has a relatively large  $\Delta_{\text{oct}}$  and both  $\text{Ru}^{3+}$  ( $d^5$ ) and  $\text{Ru}^{2+}$  ( $d^6$ ) are low-spin, differing only in extra non-bonding electron in a  $t_{2g}$  orbitals. For ground state  $\text{Ru}^{3+}$  and  $\text{Ru}^{2+}$  complexes, the Ru – N bond distance are similar.

In  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_6]^{2+}$  electron transfer occur between vibrationally excited states and greater changes

in bond lengths needed to establish the encounter complex.

**21. Sol.** b, c

In inner sphere electron transfer it is not necessary that ligand transfer take place. For self redox reaction  $\Delta G = 0$ . In inner sphere mechanism the rate of reaction depends upon polarizability of ligand.

**22. Sol.**  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  is labile and has 4 unpaired electrons, with one in the anti-bonding  $e_g$  orbitals. Occupation of this orbital renders substitution easier by leading to relatively weak chromium (4)-aqua ligand bonds.  $[\text{Cr}(\text{CN})_6]^{4-}$  is inert. It has all 4 metal valence electrons in the bonding  $t_{2g}$  levels. These orbitals are rendered bonding in character due to  $\pi$  – backbonding with cyanide ligands.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is a  $d^9$  complex, subject to Jahn-Teller distortion. Therefore, different rates are observed for exchange of axial and equatorial water molecules.

The more rapid reactivity of the Mn complex is consistent with the general observation that first substitutionally labile than second and third row complexes.